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INTERACTION VIRIAL COEFFICIENTS IN BINARY
MIXTURES OF METHANE, NITROGEN AND
CARBON DIOXIDE

BY



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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "INTERACTION VIRIAL COEFFICIENTS IN BINARY MIXTURES OF METHANE, NITROGEN AND CARBON DIOXIDE" submitted by Heng-Joo Ng in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.



ABSTRACT

An apparatus for the direct determination of the second interaction virial coefficients of mixtures has been constructed. It is a modification of the original design of Knobler.

Measurements have been made on the systems nitrogen - carbon dioxide, methane - carbon dioxide, and methane - nitrogen. The first two systems were studied over the temperature range -60°C to 120°C , while the latter was studied over the temperature range -100°C to 120°C .

The experimental results were interpreted to yield values of B_{12} . This requires a knowledge of the virial coefficients of the pure materials. For methane and nitrogen the literature values of the second virial coefficients are in good agreement. For carbon dioxide, at temperatures below 0°C , the published values of the second virial coefficient are in disagreement by as much as 15 percent. Using the present apparatus, values of the second virial coefficients of pure carbon dioxide were determined over the temperature range 0°C to -60°C .

The experimental values of the interaction virial coefficients B_{12} are in good agreement with the few literature data available.

The results were compared with predictions based on the theory of corresponding states. Both the correlation of Guggenheim and McGlashan, and the equation of Pitzer and Curl were used. For the methane - nitrogen system, the Pitzer and Curl correlation gives better agreement with this work than the correlation of Guggenheim and McGlashan. For the methane - carbon dioxide system, the Guggenheim and McGlashan correlation gives better agreement at temperatures below 300°K , while

the correlation of Pitzer and Curl gives better agreement at temperatures above 300°K. For the nitrogen - carbon dioxide system, the correlation of Guggenheim and McGlashan is in better agreement with this work.

Two common molecular potentials were considered, the Lennard-Jones and the Kihara. Published values of the parameters for the pure components were combined according to mixing rules and the interaction second virial coefficients calculated for comparison with the experimental results. For the methane - nitrogen and the methane - carbon dioxide systems, the Kihara potential gives the better prediction. For the nitrogen - carbon dioxide system, the Lennard-Jones potential is in good agreement with this work.

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NOMENCLATURE

a	Radius of the spherical molecule core
B	Second virial coefficient in the volume expansion
B'	Second virial coefficient in the pressure expansion
B_{12}	Interaction second virial coefficient
B_M	Second virial coefficient of the mixture
C	Third virial coefficient in the volume expansion
C'	Third virial coefficient in the pressure expansion
d	Density of the gas
E	Excess second virial coefficient
$F(r)$	Force of interaction between two molecules
G_1, G_2	Excess third virial coefficient
k	Boltzmann's constant
m	positive constant
n	positive constant
N	Avogadro's number
P	Pressure
P^S	Saturation vapor pressure
P_c	Critical pressure
ΔP	Differential pressure change
r	Distance between centers of two molecules
r^*	Distance between centers of two molecules when potential energy is minimum
R	Gas constant
R_1, R_2	Resistance of platinum resistance thermometer

T	Temperature
T_c	Critical temperature
U	Interaction energy between two molecules
V	Volume
V_c	Critical volume
Z_c	Critical compressibility factor

Greek

α	Positive constant
β	Positive constant
ε	Characteristic energy
μ	Universal function
σ	Characteristic molecular size parameter
ϕ	Intermolecular potential
ω	Acentric factor

Subscripts

c	Critical property
i	Component in mixture
M	Mixture

Chapter I

INTRODUCTION AND GENERAL DISCUSSION

Thermodynamic data are directly useful in process design and calculations. They are also valuable for testing correlations and methods of prediction. Although a large body of such data have become available, there is always a demand for reliable data on new systems. Such data may also be used to calculate other thermodynamic properties.

Gas phase non-ideality has been considered from a number of points of view. The virial equation of state of Onnes⁴², because of its firm theoretical basis, has often been used for calculations involving non-ideal gases. It is of the form:

$$PV = RT[1 + B(T)/V + C(T)/V^2 + \dots] \quad (1)$$

where P is the pressure, V is the molar volume, T is the absolute temperature, R is the gas constant and B and C are virial coefficients. The importance of this equation is due to the fact that it converges rapidly up to moderately high densities. It is generally possible to truncate this series at the linear term at low densities. For mixtures of gases the second virial coefficient is given by:

$$B_M = \sum_i \sum_j x_i x_j B_{ij} \quad (2)$$

similarly, the third virial coefficient is written as:

$$C_M = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} \quad (3)$$

A large number of B values have been reported in the literature^{14, 32} for pure gases and measurements of the properties of a number of large molecules have been performed but only a limited number of interaction virial coefficients have been determined. There is a clear need therefore to measure the interaction second virial coefficients over a wide range of temperature to provide the data for calculation of thermodynamic properties of mixtures. The relation of second virial coefficients to the intermolecular potential $\phi(r)$ function is as follows for a spherically symmetrical molecule

$$B = \int_0^{\infty} \left[1 - \exp\left(-\frac{\phi(r)}{kT}\right) \right] db_o(r) \quad (4)$$

where r is the distance between molecular centers and $b_o = 2\pi N r^3/3$.

It can be clearly understood that the second virial coefficient, B, is dependent on temperature on the basis of a simple physical picture. At low temperatures collisions between pairs of molecules are strongly influenced by the long-range attractive intermolecular forces, and such pairs may spend considerable time in the vicinity of one another. In this situation, a form of molecular association exists and the existence of these transient dimers causes a reduction of the pressure as predicted from the perfect gas law so B is negative. At high temperatures, the collisions of molecules are much more frequent and with higher energy; also, the weak attractive forces can only slightly influence these collisions. Instead, the short-range repulsive forces of the molecules dominate in energetic collisions. These effects give an excluded volume and produce a pressure above the perfect gas law which give the positive value of B. At still higher

temperature, the collisions become even more energetic so that molecules feel the "softness" of each other's cores, and the excluded volume effect decreases. This is the reason why second virial coefficients decrease again.

It is well-known that in the simple case, the naïve assumption, $B_{ij} = \frac{1}{2} (B_{ii} + B_{jj})$ means that there is no pressure change on mixing. But it has been pointed out by Guggenheim¹⁸ that the naïve assumption is in contrast with experiment.

Conventional methods for the study of the equation of state are difficult and required great care. For this reason, the differential techniques for determining virial coefficients have been developed. A special design for the determination of interaction virial coefficients has been developed by Knobler²⁸. In this method, at constant temperature, two identical bulbs are filled to the same pressure with different gases. A Toepler Pump is used to perform the mixing and after mixing, the pressure change is read on an oil manometer and may be directly related to the excess second virial coefficient:

$$E = B_{12} - \frac{1}{2} (B_{11} + B_{22}) \quad (5)$$

This method has been applied with success to mixtures of the permanent gases from 77 to 320°K^{3, 27, 33}. The restriction of this method is that it cannot be applied to mixtures containing condensable vapors. Gases cannot be studied if the gases are appreciably soluble in oil and mercury. Gases with the pressure above the saturation at room temperature cannot be studied because the mixing of gases by Toepler pump has to be at room temperature to reduce the vapor pressure

of mercury. The method used in this work is a modification of Knobler's²⁸ design. The detailed description will be presented in Chapter II.

Table I shows a review of all the directly measured experimental interaction second virial coefficients up to this date.

The importance of the virial equation of state lies in its theoretical connection with the forces between molecules. These forces can be considered the basic unifying element connecting a host of widely different properties; hence, it is unnecessary to measure all of the properties. In this work values of the interaction second virial coefficients, B_{12} for three binary pairs have been determined over a wide temperature range. This makes the values useful for calculations involving the virial equation of state and also allows the calculation of other thermodynamic properties over a wide range of conditions.

TABLE I

Experimental Interaction Second Virial Coefficient Data

<u>Year</u>	<u>System</u>	<u>Authors</u>	<u>References</u>
1942	$N_2 - CO_2$	Edwards and Roseveare	15
1951	$N_2 - CO_2$	Lunbeck and Boerboom	30
1953	13 binary mixtures	Michels and Boerboom	40
1953	$N_2 - CO_2$	Gorski and Miller	17
1955	$N_2 - CO_2$	Pfefferle et al.	44
1956	$CO_2 - He$	Cottrell and Hamilton	9
1956	5 binary mixtures	Cottrell, et al.	8
1959	13 binary mixtures	Knobler, et al.	27
1961	$N_2 - CO_2$ } $N_2 - CH_4$ } $CO_2 - CH_4$ }	Mason and Eakin	31
1963	$He - N_2$ } $He - Ar$ } $Ar - N_2$ }	Magasanik	33
1967	55 binary mixtures	Brewer	2
1968	15 Normal alkane ($C_1 - C_6$) mixtures	Dantzler et al.	10
1969	11 binary mixtures	Dantzler and Knobler	11
1969	9 binary mixtures	Brewer and Vaughn	4

Chapter II

EXPERIMENTAL METHODS

In this chapter, the construction of the equipment, the controlling and measuring instruments used, and the procedure for the determination of excess second virial coefficients are described. Determination of second coefficients for pure materials is also described.

A. General Survey

The principle upon which the differential method of the excess second virial coefficient is based is the fact that when two different gases which are initially at the same temperature and pressure are mixed, a pressure change will occur. Since most gaseous mixtures have negative excess second virial coefficients in this experimental temperature range, the pressure always increases upon mixing.

It has been pointed out in the previous chapter that excess second virial coefficient is $E = B_{12} - \frac{1}{2}(B_{11} + B_{22})$. The quantities determined experimentally are the filling pressure P , and the pressure difference after mixing, ΔP . The relation of ΔP with excess second virial coefficient E is as follows:

$$E = 2 \left[\frac{\Delta P}{P} - \frac{(d_1 - d_2)^2}{4d_1 d_2} \right] \frac{P}{RT d_1 d_2} + \frac{(d_1^2 - d_2^2)(C_{111}d_1 - C_{222}d_2)}{4d_1 d_2} - \frac{3}{4}(d_1 G_1 + d_2 G_2) \quad (6)$$

G_1 and G_2 are excess third virial coefficients defined by

$$G_i = C_{iij} - \frac{1}{3}(2C_{iii} + C_{jjj}) \quad (7)$$

Equation (6) is reduced upon substitution of:

$$d_i = \left\{ \frac{P}{RT} \right\} - B_{ii} \left\{ \frac{P}{RT} \right\}^2 + (2B_{ii}^2 - C_{iii}) \left\{ \frac{P}{RT} \right\}^3 + \dots \quad (8)$$

for the density of the two pure components. This then gives,

$$\begin{aligned} E = & \frac{2RT\Delta P}{P^2} - 2 \left[(B_{11} - B_{22})^2/4 - E(B_{11} + B_{22})/2 \right. \\ & + 3(G_1 + G_2)/8 \left. \right] \left\{ \frac{P}{RT} \right\} - 2 \left\{ \frac{3}{4}(B_{11} - B_{22}) \right. \\ & \left[(C_{111} - B_{11}^2) - (C_{222} - B_{22}^2) \right] + \left(\frac{E}{2} \right) (2B_{11}^2 + B_{11}B_{22} \\ & + 2B_{22}^2 - C_{111} - C_{222}) - \frac{3}{8} \left[G_1(2B_{11} + B_{22}) \right. \\ & \left. + G_2(B_{11} + 2B_{22}) \right] \left. \right\} \left\{ \frac{P}{RT} \right\}^2 + \dots \quad (9) \end{aligned}$$

from which E can be calculated by successive computer iterations.

Equation (6) was originally derived by Knobler²⁸. After making substitutions, Equation (9) has a different form from Knobler's. The detailed derivation is shown in Appendix D.

B. Experimental Equipment Construction

The apparatus consists of six main parts, namely,

- (1) Three-compartment stainless steel cylinders with identical volume.

- (2) A temperature bath assembly for low temperature and high temperature operation.
- (3) A mercury Toepler pump.
- (4) An oil and two mercury manometers.
- (5) A precision temperature indicator.
- (6) A cathetometer.

The detailed schematic flow diagram of the apparatus is shown in Figure 1. Details of the construction are as follows.

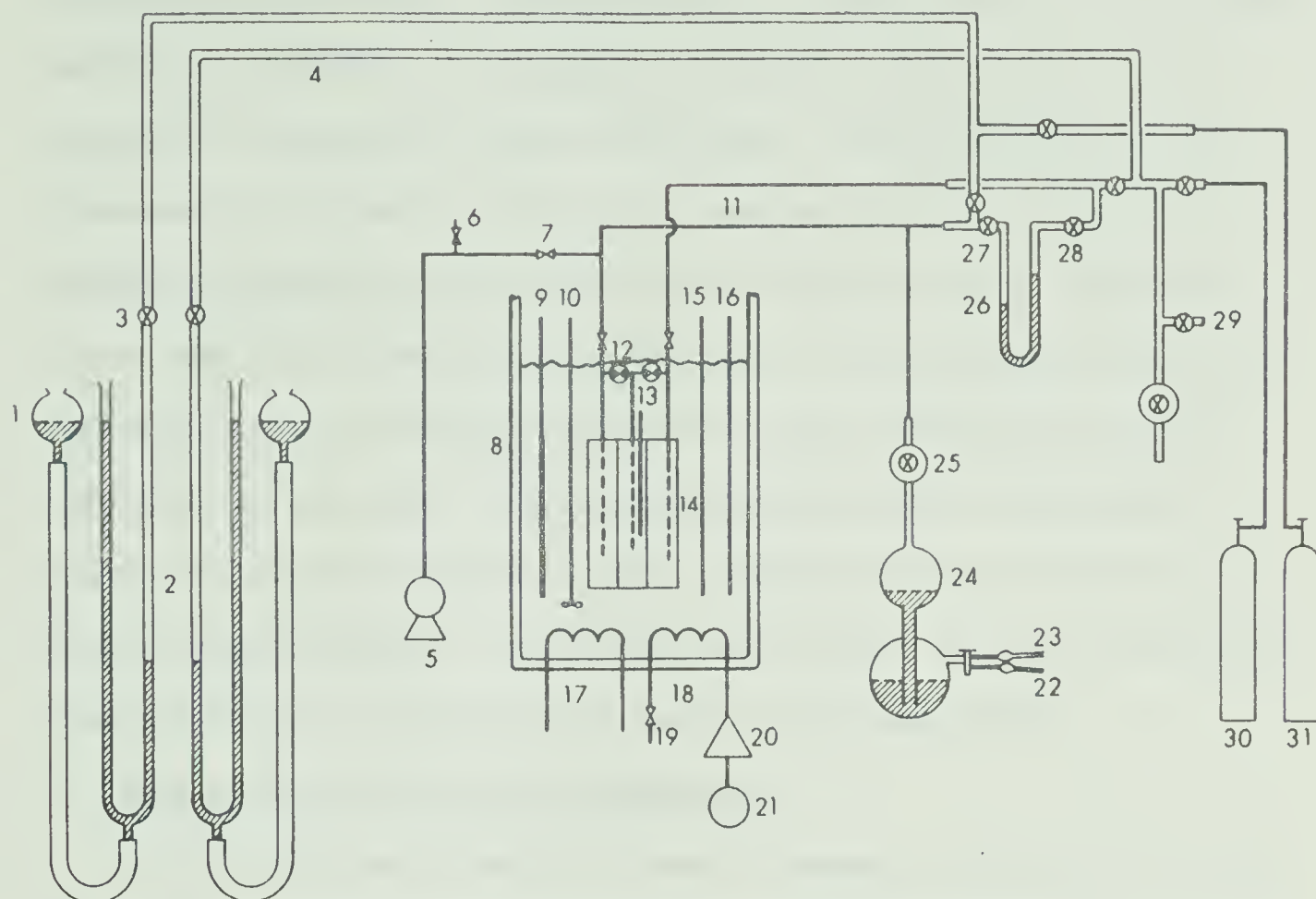
1. Gas containers

The three stainless steel cylinders were made of three 2-1/2 in. inside diameter and 13 in. long pipes. Each of the compartments has a volume of about 1000 cc and the difference between the three volumes is within 0.1 percent. These three cylinders were oriented 120 degrees to a center small tube in which the platinum resistance thermometer is placed. The three cylinders were connected to 2 mm. glass capillary tubing by means of 1/8 in. O.D. stainless steel tubing outside of the bath and 1/4 in. O.D. stainless steel tubing inside the bath. The stainless steel tubing extended nearly to the bottom of each cylinder. The sections of the tubing within the cylinders had holes drilled in their walls to make the flushing and charging and mixing of the gases more efficient.

Two of the valves which are immersed in the fluid are stainless steel bellows valves (Hoke Inc., type 4212 F4Y). The other valves used are screwed bonnet valves (Whitey Research Tool Co.).

2. Temperature bath

It is necessary to maintain a constant temperature within 0.01°C



LEGEND

- | | |
|--|--|
| 1. Levelling bulbs | 16. Sensor for the refrigerator |
| 2. Mercury manometer | 17. Refrigerator |
| 3. Stopcock | 18. Liquid nitrogen cooler |
| 4. Glass tubing | 19. Nitrogen vapor exhaust control valve |
| 5. Vacuum pump | 20. Liquid nitrogen Dewar (50 l.) |
| 6. Vacuum release valve | 21. Pressure reducer |
| 7. Vacuum valve | 22. Air pressure line |
| 8. Constant temperature bath | 23. Air release line |
| 9. Heater | 24. Toepler pump |
| 10. Stirrer | 25. Toepler pump stopcock |
| 11. Stainless steel tubing (1/8 in. O.D.) | 26. Oil manometer |
| 12. Bellows valves | 27, 28. Oil manometer stopcocks |
| 13. Platinum resistance thermometer | 29. Vent |
| 14. Stainless steel cylinders (gas containers) | 30. A gas container |
| 15. Sensor for the heat input controller | 31. B gas container |

Figure 1. Schematic Diagram of the Apparatus

during the experiment. For this purpose a steel bath was constructed and 4 in. thickness of fibreglass is used for insulation. The net capacity of the bath is about 170 liters. The platinum resistance thermometer is placed at the center part of the bath to measure the absolute temperature. The temperature controller used a thermistor probe as a sensor and heater of 750 watts. For the high temperature operation, air is flowing in the 1/2 in. O.D. copper coil which is installed in the bath. For temperatures below room temperature operation, liquid nitrogen is used. The bath was well-stirred by a single-stage impeller. The fluids used are Esso-10-W oil for higher temperature and ethanol for the temperatures below 20°C.

C. Measuring and Controlling Instruments

The instruments which are used to measure and control various valves to carry out this experiment are described briefly.

1. The absolute temperature in the bath was determined by two platinum resistance thermometers and a high precision inductive ratio arm bridge (Automatic Systems Laboratories). One of the platinum resistance thermometers is placed in the bath and the other one is placed in the ice dewar as a reference. The indicated ratio from the bridge is $\eta = \frac{R_1}{R_1 + R_2}$, where R_1 is the reference platinum resistance thermometer and R_2 is the one in the bath. The calibrations of the platinum resistance thermometers are presented in Appendix A.

2. The filling pressure is measured by means of a mercury manometer. The pressure difference after mixing is measured with an oil manometer by means of a precision cathetometer (W.G. Pye & Co. Ltd.). The determination of the oil density is presented in Appendix A.

3. The bath temperatures were controlled within $\pm 0.01^{\circ}\text{C}$ by a temperature controller (Hallikainen Instruments).

4. The refrigeration unit (Cincinnati Sub-Zero products) was used to maintain constant temperatures overnight.

D. Experimental Procedure

When the temperature equilibrium between the bath and the cylinders was being attained, several successive flushings of the Toepler pump with a 50-50 mixture of the gases at 2 atm. under study were made. The stopcock to the Toepler pump was closed. After four successive evacuations and flushings with one of the components, two of the cylinders were charged to about 2 atm. Then with three more evacuations and flushings of the third cylinder, it was charged with the second component. The pressure of the gases in the cylinders can be read from the mercury manometer and approximately equalized by using the mercury levelling bulbs with the aid of the oil manometers.

After one hour, the gases in the cylinders attained the equilibrium temperature with the bath. The stopcocks of the oil manometer are opened, once again the pressure of two different gases can be equalized by the levelling bulbs. The oil manometer is isolated again, then the stopcock to the Toepler pump is opened and the mercury level is pressed back by the outside air line to the fiducial mark. The small differential pressure was read by the cathetometer and the reading recorded as the initial differential pressure.

One of the two cylinders which had the same gas was then isolated for use as a reference pressure and the oil manometer was isolated again. The mixing of the two pure gases was accomplished by

operating the Toepler pump for 60 cycles. The operation of the Toepler pump was performed automatically by a relay unit and a solenoid valve on the air line. The mercury level was then brought back to the fiducial mark manually and the Toepler pump stopcock was closed. After opening the oil manometer stopcock, the differential pressure after mixing was read.

To make sure of the complete mixing, the Toepler pump was operated for another five cycles and it was found that the same pressure difference was read for most of the cases. Then the reading was accepted as the final differential pressure after mixing. The actual differential pressure is simply the difference between the final and initial reading. The experimental run was replicated with every temperature.

A small part of the gases under study are exposed to room temperature. Serious error will occur when the volume of gas at the controlled temperature and the volume of gas at room temperature are comparable. For this design, only 0.47 percent of the volume of the gas is exposed to room temperature. The tubing from the bath to the Toepler pump and the oil manometer was made as short as possible. Stainless steel tubing of 1/8 in. O.D. and 2 mm. I.D. capillary glass tubing were used for this purpose.

This experiment cannot be carried out at higher pressures because the third virial coefficient of the pure component will affect the differential pressure after mixing and increase the experimental error.

E. Experimental Determination of the Second Virial Coefficient of Carbon Dioxide

The second virial coefficient of carbon dioxide below 0°C has been determined in this work because of the disagreement of the data in the literature.

The same apparatus which has been used for measuring interaction second virial coefficients was used. It was accomplished by measuring the change in pressure that occurs between helium and carbon dioxide when the temperature is varied. This determination permits the calculation of the change in the second virial coefficients with temperature. One value of the second virial coefficient at the reference temperature must be known. In this work, $B_{\text{CO}_2} = -150 \text{ cc/gm-mole}$ at 0°C was used.

The virial equation of state is used for the calculation and the method of calculation is presented in Appendix E.

These new determinations of the second virial coefficient for pure carbon dioxide are given in Table V.

F. Purity of Gases

The sources and purity of the gases used are given in Table II. The gases were used without further purification.

TABLE II

Sources and Purity of the Gases Used

1. Nitrogen (high purity)

Supplier: Consumer's Welding Co.

Typical Analytical Data:

Nitrogen	99.993 mole %
Oxygen	20 ppm
Carbon dioxide	5 ppm
Hydrogen	5 ppm
Moisture	15 ppm
Argon	100 ppm
Maximum total impurities (non-inert)	40 ppm

2. Methane (ultra pure)

Supplier: Matheson Gas Products

Actual Analytical Data:

Methane	99.97%
Carbon dioxide	< 10 ppm
Oxygen	9 ppm
Nitrogen	24 ppm
Ethane	35 ppm
Propane	< 5 ppm

3. Carbon Dioxide

Supplier: Canadian Liquid Air Co. Ltd.

Typical Analytical Data:

Carbon dioxide	99.95% by volume
Sulfur compounds	0 ppm
Carbon monoxide	0 ppm

TABLE II (continued)

	Oil	5 ppm
	Balance	inerts

4. Helium

Supplier: Canadian Liquid Air Co. Ltd.

Purity: 99.995%

Chapter III

EXPERIMENTAL RESULTS AND THEIR COMPARISON

This chapter covers the experimental results and the comparison of this work with other experimental work in the literature.

The second interaction virial coefficients are calculated from the second and third virial coefficients of the pure gases. In section A, the virial coefficients of the pure gases are listed.

In section B, experimental results of the excess second virial coefficient and interaction second virial coefficients for three systems, methane - nitrogen, methane - carbon dioxide, and nitrogen - carbon dioxide are reported. The comparison with other experimental values is made in this section.

A. Pure Component Virial Coefficients

1. Second and third virial coefficients of methane

Second virial coefficients obtained by different sets of workers are all in good agreement. A smooth curve through all the data was prepared by Dymond and Smith¹⁴ in 1969. This curve agrees well with that reported by Goodwin¹⁶ in 1970.

The reported third virial coefficients of methane are not in good agreement with each other. For temperatures below 0°C, very few sets of the data can be compared. The values used in this work are the smoothed values from several workers in the literature^{2,13,22,35,36,48}. The listing of the second and third virial coefficients of methane used for this work is presented in Table III.

TABLE III

Second and Third Virial Coefficients of Methane

<u>Temperature ($^{\circ}\text{K}$)</u>	<u>B (cc/gm-mole)</u>	<u>C (cc²/gm-mole²)</u>
173.15	-145.0	4900
193.15	-116.0	4300
213.15	- 94.5	3860
233.15	- 78.0	3450
253.15	- 65.0	3050
273.15	- 54.5	2700
293.15	- 45.0	2600
313.15	- 37.5	2390
333.15	- 31.0	2250
353.15	- 26.0	2140
373.15	- 21.0	2120
393.15	- 16.5	1880

2. Second and third virial coefficients of nitrogen

Values of the second virial coefficient of nitrogen which have been reported generally agree to within the estimated experimental uncertainties. A smooth curve through all the data is also prepared by Dymond and Smith¹⁴. The third virial coefficients obtained by different sets of workers agree well. Smoothed values from these workers^{6,23,37,38,43} are used. Table IV shows the second and third virial coefficients of nitrogen which are used in this work.

3. Second and third virial coefficients of carbon dioxide

At temperatures above 200°K, the second virial coefficients reported by Dadson et al.^{5,12} are significantly less negative than those obtained by most other workers^{7,34,39}. It is not possible to say which set of data is the more accurate. At temperatures below 250°K there is a marked discrepancy among the results of Schäfer⁴⁹, and Cook⁷ and Brewer². The values of the interaction second virial coefficients will depend on the pure second virial coefficients that have been chosen. The values between 270 and 400°K for this work are the smooth curve based on Michels and Michels³⁹, MacCormack and Schneider³⁴ and Brewer² because these data are in good agreement. The values below 270°K had been determined by this work and are in good agreement with Brewer. Figure 2 shows the comparison and the smooth curve used in this work.

The reported third virial coefficients of carbon dioxide is even more scarce especially for temperatures below 0°C. A smooth curve from Brewer², Michels and Michels³⁹ and Butcher and Dadson⁵ is used in this work.

TABLE IV
Second and Third Virial Coefficients of Nitrogen

<u>Temperature (^oK)</u>	<u>B (cc/gm-mole)</u>	<u>C (cc²/gm-mole²)</u>
173.15	-51.0	2250
193.15	-39.0	2000
213.15	-29.0	1900
233.15	-21.5	1800
253.15	-15.5	1700
273.15	-10.5	1500
293.15	- 5.8	1250
313.15	- 2.0	1250
333.15	+ 1.0	1250
353.15	+ 3.8	1200
373.15	+ 6.0	1200
393.15	+ 8.2	1150

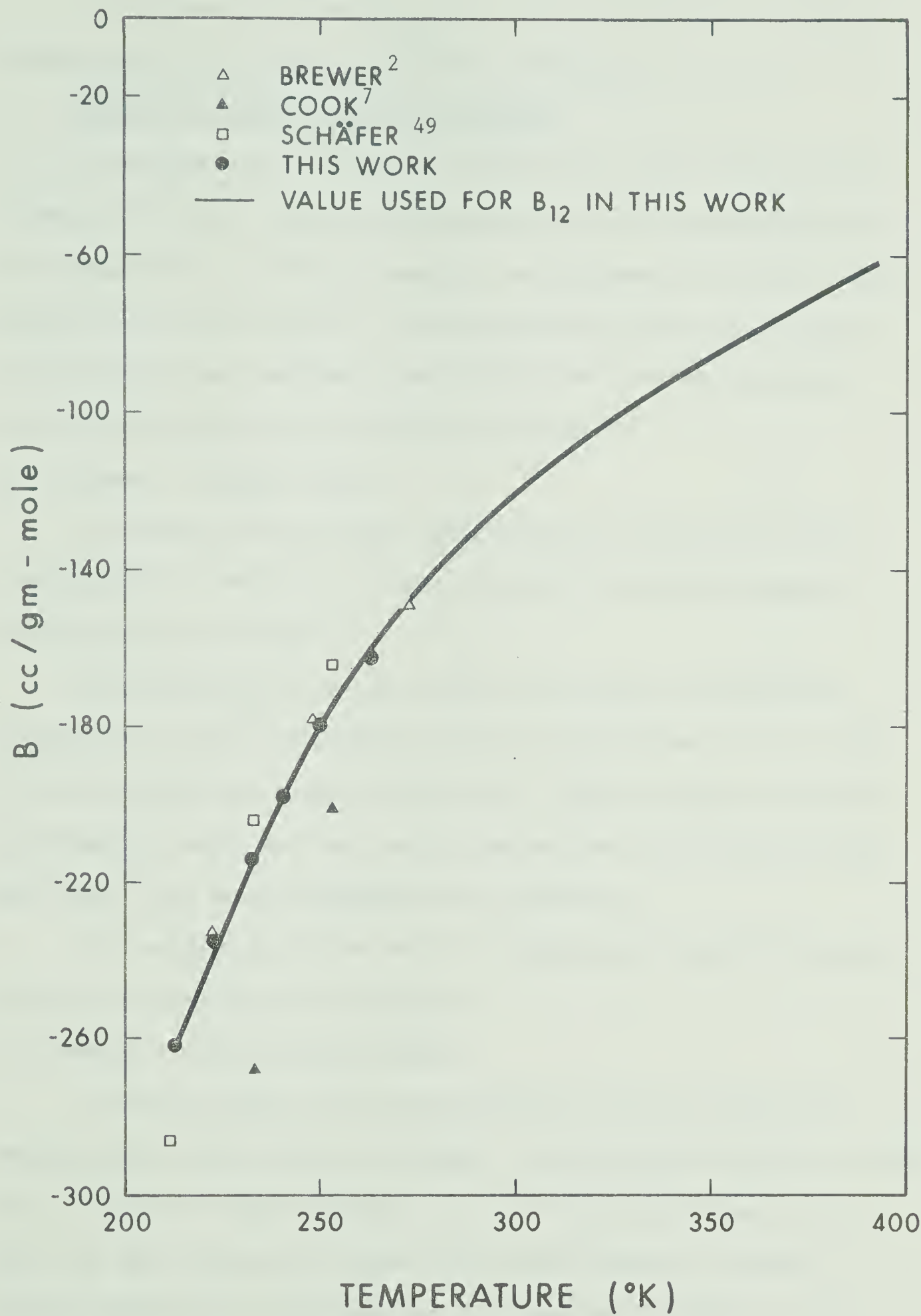


Figure 2. Second Virial Coefficients of CO_2

The values of second and third virial coefficients of carbon dioxide used in this work are listed in Table V.

B. Interaction Second Virial Coefficients

The experimental results of interaction second virial coefficients of the three systems are presented in this section. The raw data which show the filling pressure, the differential pressure after mixing, the excess quantity, E , the second and third virial coefficients of the pure components, and finally the interaction second virial coefficients are presented in Appendix B.

1. Methane - Nitrogen System

The excess second virial coefficient and interaction virial coefficients of methane - nitrogen mixtures at individual temperatures are given in Table VI.

The experimental results from other workers and calculated interaction virial coefficients from the extrapolation of P-v-T data of other workers are shown in Table VII. Figure 3 shows that Brewer's experimental result and the results derived from P-v-T data of Keyes and Burks²⁴ are in good agreement with this work.

No comparisons can be made for temperatures below 0°C because no data are available in literature.

2. Methane - Carbon Dioxide System

Table VIII shows the excess quantities and the interaction second virial coefficients of methane - carbon dioxide mixtures of this work. The P-v-T data of Reamer, et al.⁴⁷ have been extrapolated to give B_M , then interaction second virial coefficients of methane - carbon dioxide were calculated and are presented in Table IX. The

TABLE V

Second and Third Virial Coefficients of Carbon Dioxide

<u>Temperature ($^{\circ}$K)</u>	<u>B (cc/gm-mole)</u>	<u>C (cc²/gm-mole²)</u>
213.15	-262.0	1000
233.15	-214.0	4700
253.15	-180.0	5600
273.15	-150.0	5750
293.15	-127.0	4600
313.15	-110.0	4600
333.15	- 95.0	4400
353.15	- 83.5	3900
373.15	- 73.0	3400
393.15	- 62.0	2900

TABLE VI

Excess and Interaction Second Virial Coefficients of the

Methane - Nitrogen System

<u>Temperature (^oK)</u>	<u>E (cc/gm-mole)</u>	<u>B₁₂ (cc/gm-mole)</u>
173.15	10.67	-87.32
193.15	9.45	-68.05
213.15	7.84	-53.91
233.15	7.38	-42.36
253.15	6.83	-33.42
273.15	5.78	-26.72
293.15	5.81	-19.58
313.15	4.62	-15.12
333.15	4.41	-10.59
353.15	3.95	- 7.14
373.15	2.31	- 5.14
393.15	1.68	- 2.47

TABLE VII

Interaction Second Virial Coefficients of the Methane -
Nitrogen System From the Literature

<u>Temperature ($^{\circ}$K)</u>	<u>Brewer</u> ²	<u>Mason and Eakin</u> ³¹	<u>Keyes and Burks</u> ²⁴
273.15	-25.72		-26.59
288.50		-16.8	
313.15			-16.11
353.15			- 5.66

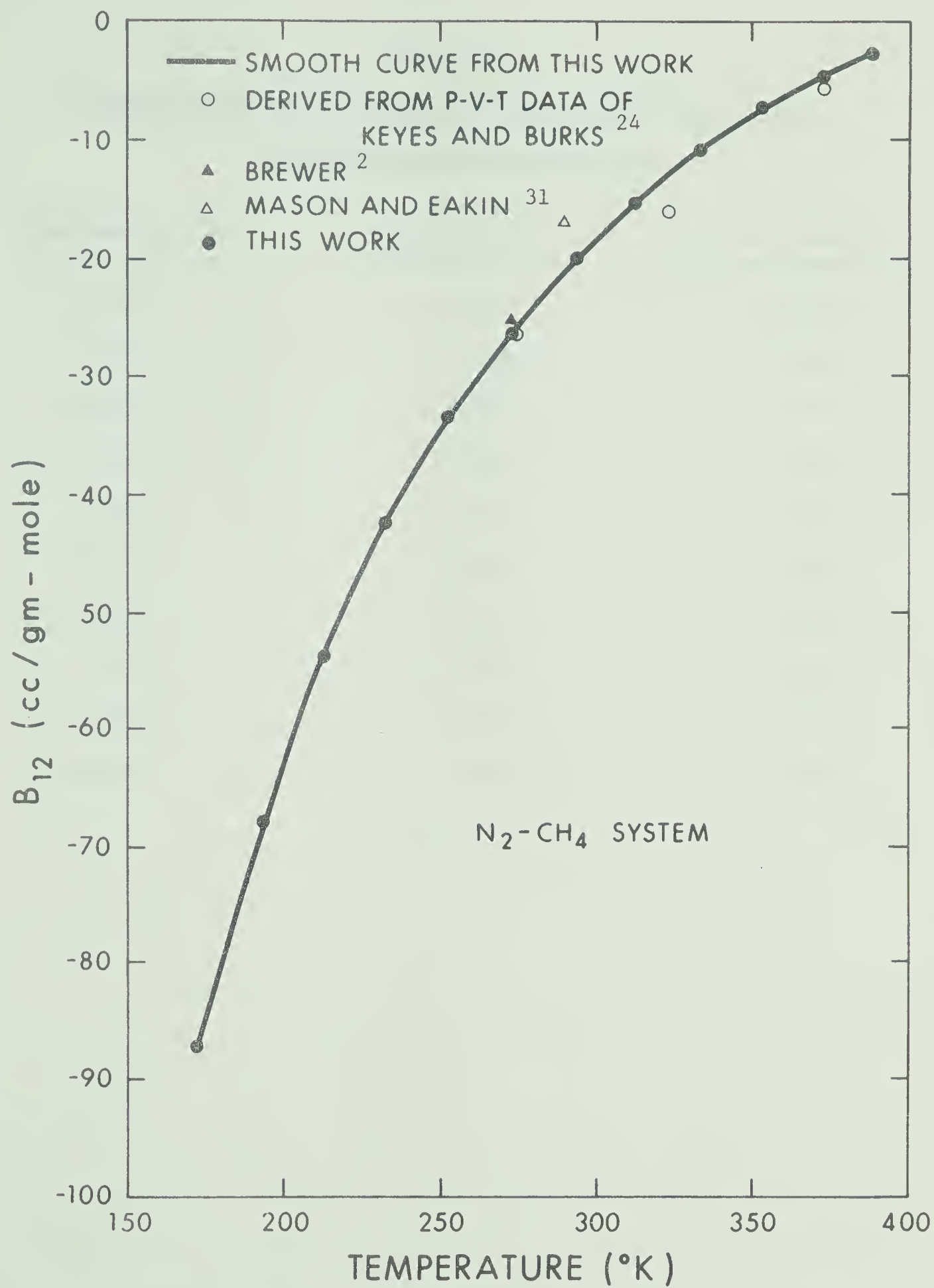


Figure 3. Comparison of Experimental Results

TABLE VIII

Excess and Interaction Second Virial Coefficients of the

Methane - Carbon Dioxide System

<u>Temperature (^oK)</u>	<u>E (cc/gm-mole)</u>	<u>B₁₂ (cc/gm-mole)</u>
213.15	41.51	-136.74
233.15	31.05	-114.94
253.15	25.95	- 97.55
273.15	21.00	- 81.24
293.15	18.74	- 67.25
313.15	16.42	- 57.33
333.15	14.51	- 48.49
353.15	11.62	- 43.14
373.15	10.43	- 36.56
393.15	5.98	- 33.26

interaction second virial coefficients determined by other workers in the literature are also shown in Table IX.

Zaalishvili⁵¹ presents values of interaction second virial coefficients for methane - carbon dioxide. From the P-v-T data of Reamer, et al.⁴⁷, Zaalishvili⁵¹ calculated values for the second virial coefficient of methane - carbon mixture. The interaction second virial coefficient values are calculated by using second virial coefficients of methane from his previous work⁵⁰, and carbon dioxide from MacCormack and Schneider³⁴. These values are also given in Table IX.

Figure 4 shows the comparison of the values presented in Table IX with this work. Interaction second virial coefficients derived from Reamer, et al by this work are in good agreement with this experimental work. Due to the different values of pure second virial coefficients of methane used by Zaalishvili, the interaction second virial coefficients of Zaalishvili are slightly different from those derived by this work. They are in good agreement with this experimental work because the second virial coefficient of methane used is little different from that used in this work.

At temperatures below 0°C, there are no reported results from the literature, so no comparison can be made.

3. Nitrogen - Carbon Dioxide System

The experimental results of this work are listed in Table X. Table XI presents the experimental results determined by other workers, and the extrapolated results from the P-v-T data of Haney and Bliss²⁰. Figure 5 shows that results derived from P-v-T data of Haney and Bliss are in very good agreement with this work.

TABLE IX

Interaction Second Virial Coefficient of the Methane -
Carbon Dioxide System From the Literature

<u>Temperature</u>	<u>Reamer et al</u> ⁴⁷	<u>Zaalishvili</u> ⁵¹	<u>Brewer</u> ²	<u>Mason and Eakin</u> ³¹
273.15			-77.55	
288.50				-59.40
311.0	-57.42	-63.2		
344.0	-43.39	-48.2		
377.0	-32.36	-36.6		
411.0	-22.08	-19.8		

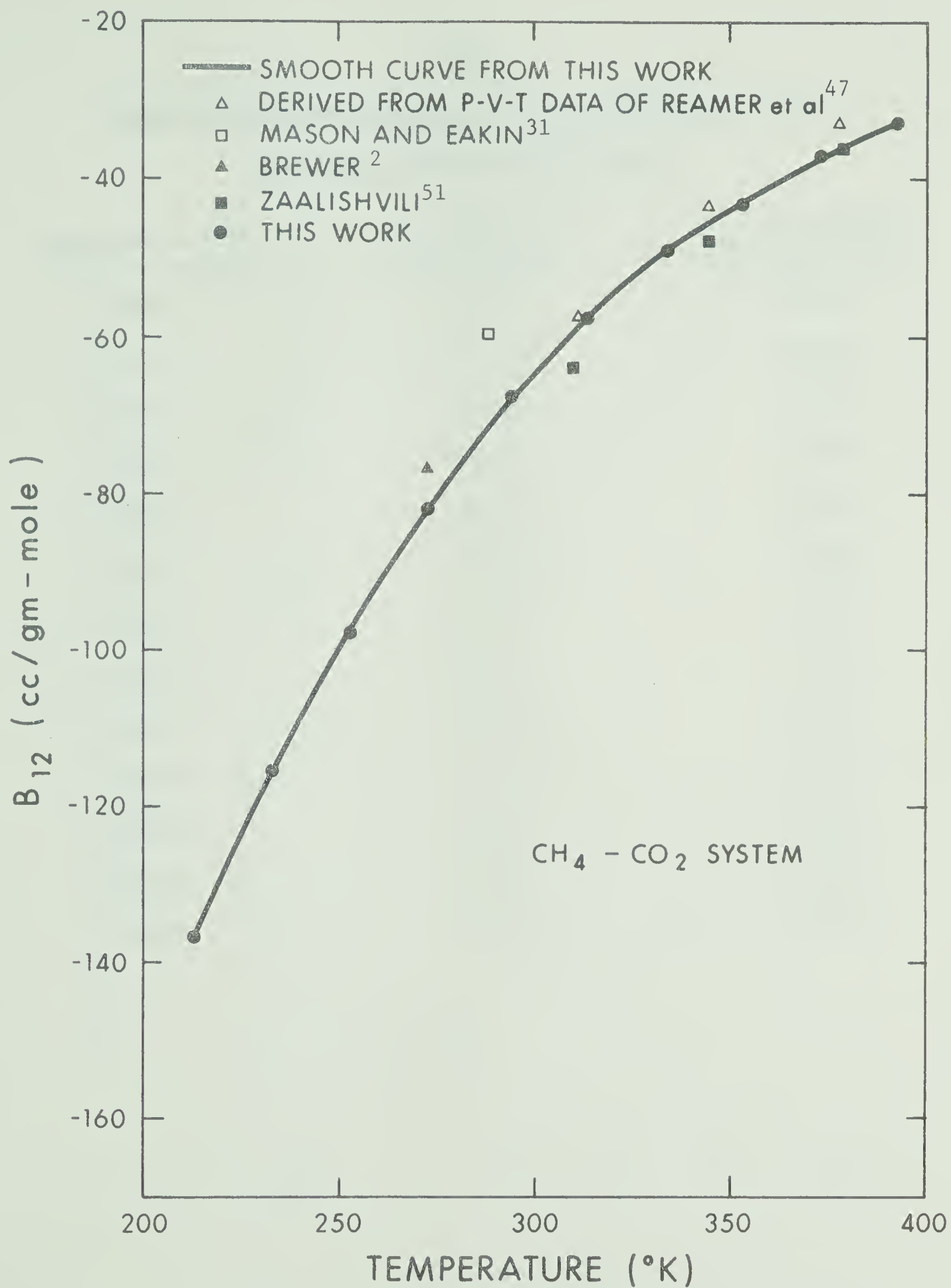


Figure 4. Comparison of Experimental Results

TABLE X

Excess and Interaction Second Virial Coefficient of the

Nitrogen - Carbon Dioxide System

<u>Temperature (°K)</u>	<u>E (cc/gm-mole)</u>	<u>B₁₂ (cc/gm-mole)</u>
213.15	50.35	-95.14
233.15	33.75	-83.99
253.15	28.81	-68.93
273.15	22.96	-57.28
293.15	20.70	-45.70
303.15	20.03	-40.98
313.15	18.74	-37.26
323.15	17.71	-33.28
333.15	16.52	-30.47
348.15	15.32	-26.18
363.15	13.40	-22.91
373.15	12.58	-20.71
393.15	11.34	-15.56

TABLE XI

Interaction Second Virial Coefficients of the Nitrogen -

Carbon Dioxide System From the Literature

Temperature (°K)	Haney and 20 Bliss	Brewer ²	Cottrell ⁸ et al	Pfefferle ⁴⁴ et al	Gorski and 17 Miller	Edwards and 15 Roseveare	Lunbeck and 30 Boerboom	Michels and 40 Boerboom
223.15		-77.45						
248.15		-59.75						
273.15		-50.88						
298.15	-43.93					-47.78	-42.6	-43.42
303.15			-41.6±6.2	-36.47	-36.58			
323.15	-33.37							
333.15			-36.0±4.0					
348.15	-26.37							
363.15			-28.5±3.6					
373.15	-20.82							
398.15	-13.09							

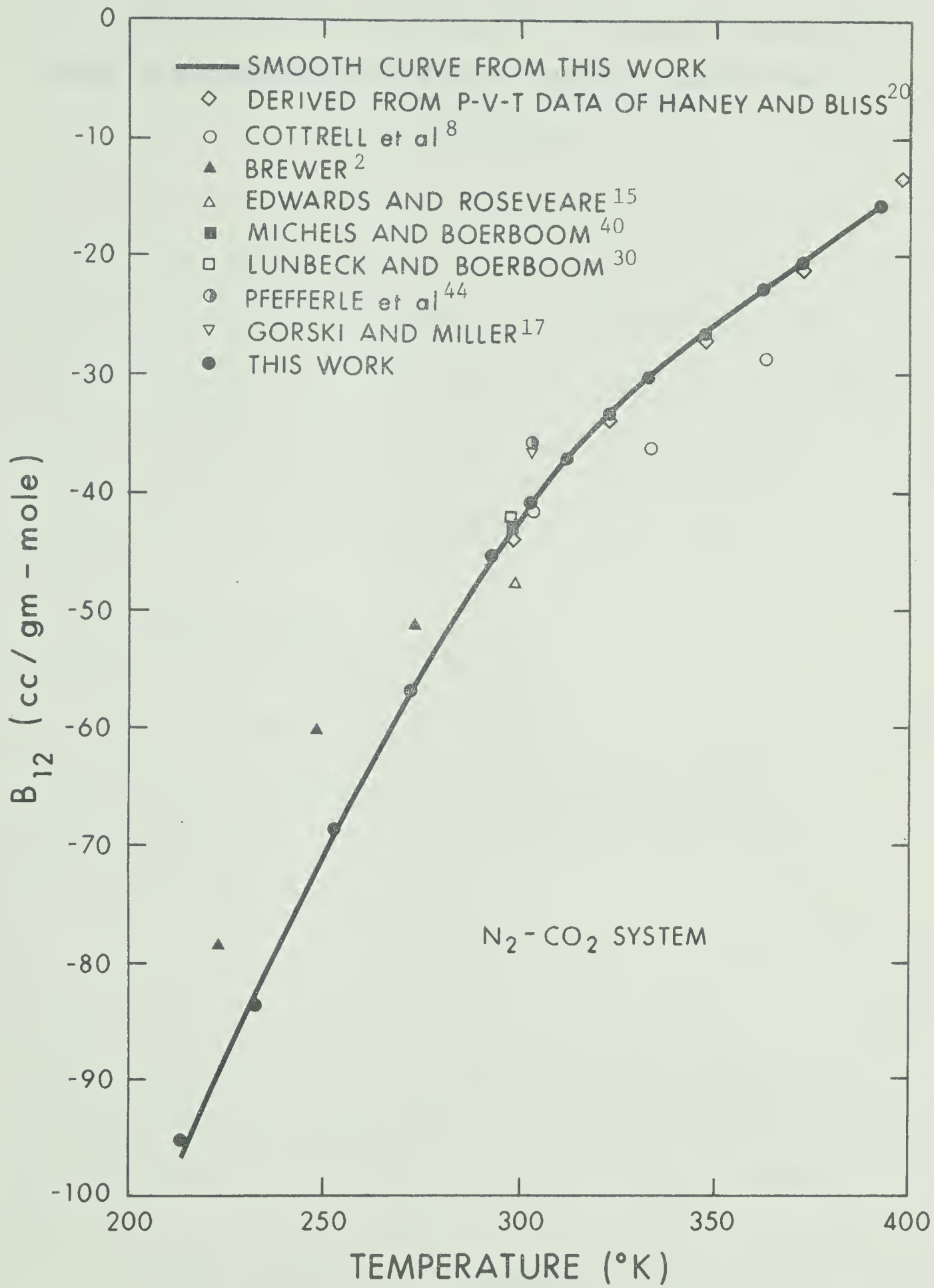


Figure 5. Comparison of Experimental Results

For temperatures lower than 0°C , only two data points from Brewer² are available, which are less negative than this work.

CHAPTER IV

THEORETICAL PREDICTIONS OF INTERACTION SECONDVIRIAL COEFFICIENTS

The calculation of interaction second virial coefficients by means of the principle of corresponding states and molecular potentials are performed in this chapter. For corresponding states, interaction second virial coefficients calculated from the Guggenheim and McGlashan¹⁹ and Pitzer and Curl⁴⁵ correlations are compared with this work. For molecular potentials, the comparison between this work and values calculated from the Lennard-Jones and Kihara potentials is also made.

A. Corresponding States

1. Guggenheim and McGlashan Correlation

In order that a substance conforms to the principle of corresponding states, the assumption that the interaction energy, U , between two molecules with distance apart of r can be completely defined by the simple relation as

$$\frac{U}{\epsilon} = \mu \left(\frac{r}{\sigma} \right) \quad (10)$$

Where ϵ is an energy and σ is a length both characteristic of the molecule, and μ is the universal function for all the molecules concerned. Upon substitution, Equation (4) can then be written in dimensionless form

$$\frac{B}{2\pi N\sigma^3} = \int_0^\infty \left[1 - \exp \left(- \frac{\epsilon \mu(r/\sigma)}{kT} \right) \right] \left(\frac{r}{\sigma} \right)^2 d \left(\frac{r}{\sigma} \right) \quad (11)$$

If σ^3 is set proportional to the critical volume V_c and ϵ/k proportional to the critical temperature T_c , then

$$\frac{B}{V_c} = F\left(\frac{T}{T_c}\right) \tag{12}$$

where F is a universal function of the reduced temperature. The curve for equation (12) had been prepared by Guggenheim and McGlashan¹⁹ from data on pure material. Equation (12) can be applied to a binary mixture, with semi-empirical mixing rules for the characteristic parameters as

$$V_{c_{ij}} = \frac{1}{8} (V_{c_i}^{1/3} + V_{c_j}^{1/3}) \tag{13}$$

and

$$T_{c_{ij}} = (T_{c_i} \cdot T_{c_j})^{1/2} \tag{14}$$

The interaction second virial coefficient is then calculated by means of equation (2).

2. The Correlation of Pitzer and Curl

Pitzer proposed a third parameter for the corresponding states. He defined an acentric factor ω , which is a macroscopic measure of the extent to which the force field around a molecule deviates from spherical symmetry. The operational definition of ω is given as

$$\omega = -\log_{10}\left(\frac{P^s}{P_c}\right)_{T/T_c = 0.7} - 1.0000 \tag{15}$$

where P^S is the saturation vapor pressure. When applied to the second virial coefficient, the extended theory of corresponding states asserts that for all fluids in the same class,

$$\frac{B}{N\sigma^3} = F_{\omega}\left(\frac{kT}{\epsilon}\right) \quad (16)$$

where σ is a characteristic molecule size, and ϵ/k is a characteristic energy expressed in units of temperature. The function F_{ω} depends on the acentric factor ω .

Pitzer and Curl have rewritten equation (16) by replacing σ and ϵ/k with macroscopic parameters as

$$\frac{BP_c}{RT_c} = F_{\omega}\left(\frac{T}{T_c}\right) \quad (17)$$

and investigated the dependence of F_{ω} on acentric factor at constant reduced temperature. Within the limits of experimental information then available, F_{ω} is a linear function of ω , thus:

$$\frac{BP_c}{RT_c} = F^{(0)}\left(\frac{T}{T_c}\right) + \omega F^{(1)}\left(\frac{T}{T_c}\right) \quad (18)$$

where

$$\begin{aligned} F^{(0)}\left(\frac{T}{T_c}\right) = & 0.1445 - 0.330\left(\frac{T}{T_c}\right)^{-1} - 0.1385\left(\frac{T}{T_c}\right)^{-2} \\ & - 0.0121\left(\frac{T}{T_c}\right)^{-3} \end{aligned}$$

$$F^{(1)}\left(\frac{T}{T_c}\right) = 0.073 + 0.46\left(\frac{T}{T_c}\right)^{-1} - 0.50\left(\frac{T}{T_c}\right)^{-2} - 0.097\left(\frac{T}{T_c}\right)^{-3} \\ - 0.0073\left(\frac{T}{T_c}\right)^{-8}$$

This correlation was extended to mixtures with the following equations:

$$P_{c_{12}} = \frac{Z_{c_{12}}^R T_{c_{12}}}{V_{c_{12}}} \quad (19)$$

$$Z_{c_{12}} = 0.271 - 0.08\omega_{12} \quad (20)$$

The mixing rules as

$$\omega_{12} = \frac{1}{2}(\omega_1 + \omega_2) \quad (21)$$

and equation (13) and (14).

3. Comparison of Results

The calculated results of interaction second virial coefficients from corresponding states of Guggenheim and McGlashan and the calculation of the Pitzer and Curl correlation are shown in Tables XII, XIII, and XIV and the values are plotted on Figures 6, 7 and 8 for the methane - nitrogen, methane - carbon dioxide and nitrogen - carbon dioxide systems respectively.

For methane - nitrogen systems, the predicted results from Pitzer and Curl correlation are slightly more negative for temperatures lower than 350°K but less negative at temperatures higher than 350°K in comparison with this work. The Guggenheim and McGlashan prediction is always more negative than this work.

TABLE XII

Interaction Second Virial Coefficients of Methane - Nitrogen
Mixtures From This Work, Guggenheim and McGlashan Correlation
and, Pitzer and Curl Correlation

<u>Temperature</u>	<u>This Work</u>	<u>Guggenheim</u>	<u>Pitzer</u>
173.15	-87.32	-89.8	-88.28
193.15	-68.05	-69.0	-70.06
213.15	-53.91	-56.0	-56.01
233.15	-42.36	-45.4	-44.86
253.15	-33.42	-36.9	-35.82
273.15	-26.72	-30.2	-28.36
293.15	-19.58	-23.6	-22.09
313.15	-15.12	-18.9	-16.75
333.15	-10.59	-14.2	-12.16
353.15	- 7.14	- 9.45	- 8.17
373.15	- 5.14	- 6.63	- 4.67
393.15	- 2.47	- 3.78	- 1.58

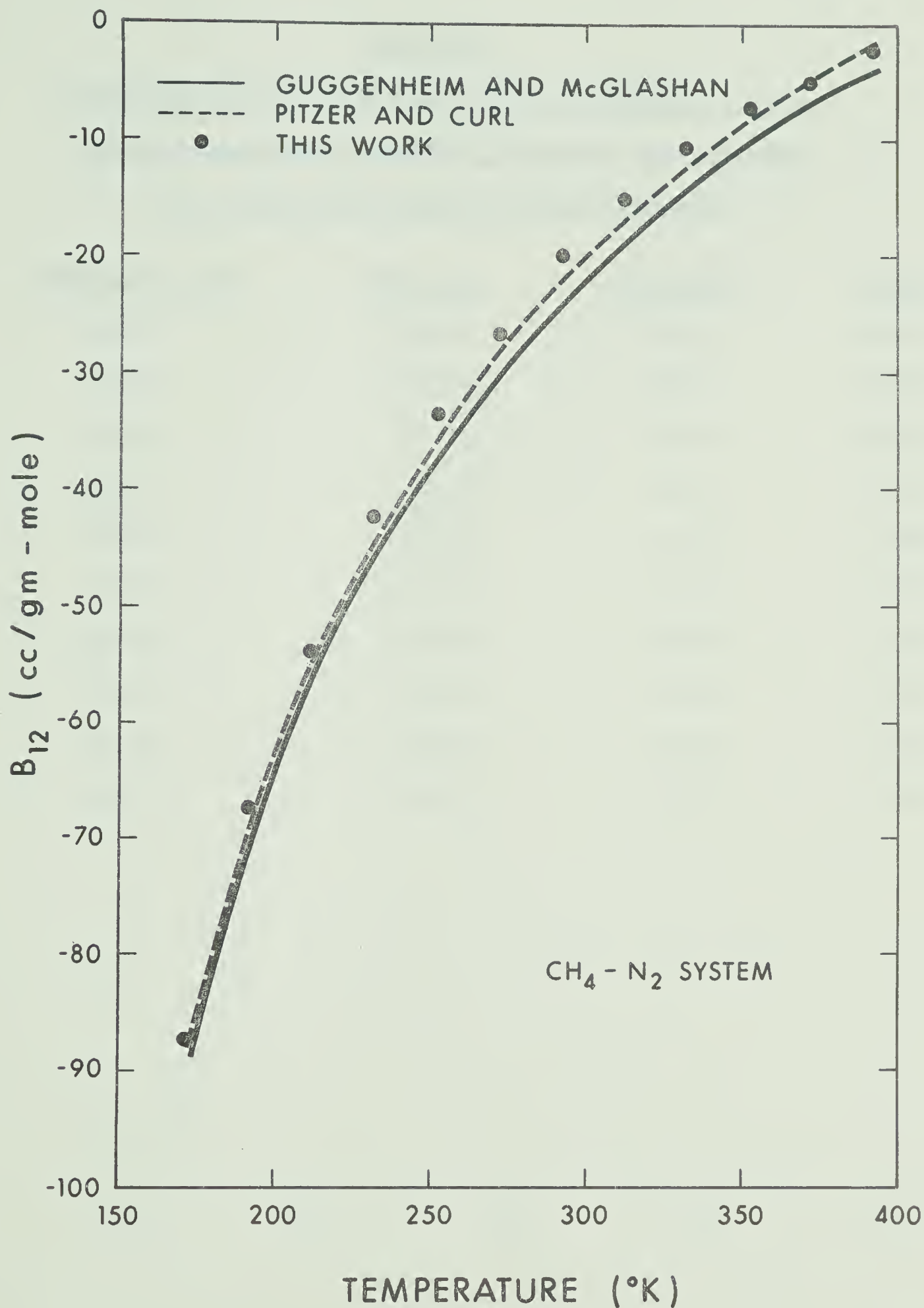


Figure 6. Comparison of B_{12} With Values Calculated From Corresponding States

TABLE XIII

Interaction Second Virial Coefficients of Methane - Carbon
Dioxide Mixtures From This Work, Guggenheim and McGlashan
Correlation and Pitzer and Curl Correlation

<u>Temperature (^oK)</u>	<u>This Work</u>	<u>Guggenheim</u>	<u>Pitzer</u>
213.15	-136.74	-158.0	-164.41
233.15	-114.94	-120.0	-133.58
253.15	- 97.55	- 99.0	-109.71
273.15	- 81.24	- 86.5	- 90.73
293.15	- 67.25	- 74.0	- 75.32
313.15	- 57.33	- 63.4	- 62.59
333.15	- 48.49	- 56.6	- 51.92
353.15	- 43.14	- 48.0	- 42.87
373.15	- 36.56	- 43.2	- 35.11
393.15	- 33.26	- 36.5	- 28.39

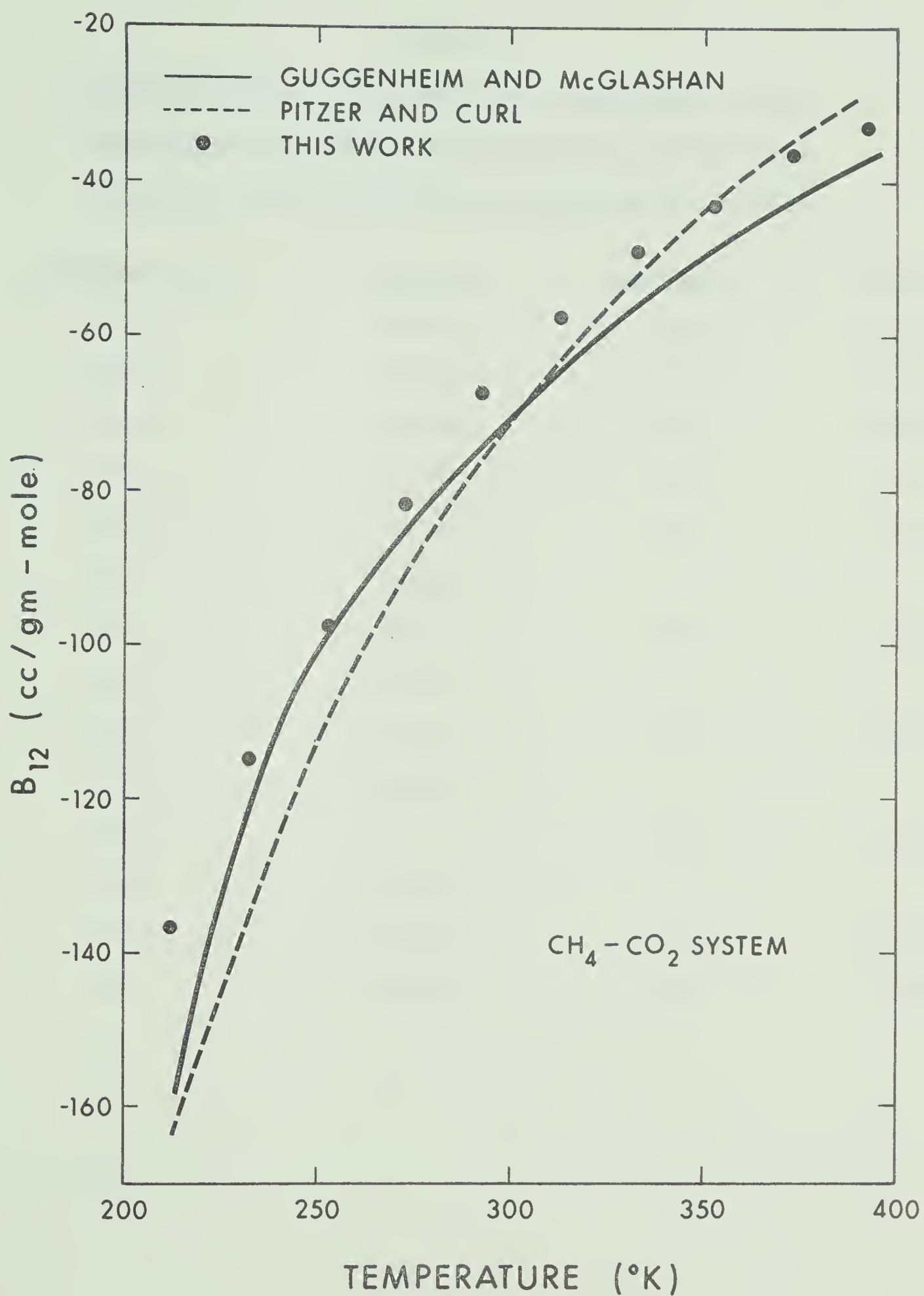


Figure 7. Comparison of B_{12} With Values Calculated from Corresponding States

TABLE XIV

Interaction Second Virial Coefficient of Nitrogen - Carbon
Dioxide Mixtures From This Work, Guggenheim and McGlashan
Correlation and Pitzer and Curl Correlation (cc/gm-mole)

<u>Temperature (^oK)</u>	<u>This Work</u>	<u>Guggenheim</u>	<u>Pitzer</u>
213.15	-95.14	-92.0	-96.39
233.15	-83.99	-73.5	-76.49
253.15	-68.93	-62.5	-60.88
273.15	-57.28	-53.4	-48.34
293.15	-45.70	-45.0	-38.09
303.15	-40.98		
313.15	-37.26	-37.8	-29.56
323.15	-33.28		
333.15	-30.47	-32.1	-22.38
348.15	-26.18		
353.15		-28.4	-16.26
363.15	-22.91		
373.15	-20.71	-23.0	-10.99
393.15	-15.56	-18.4	- 6.41

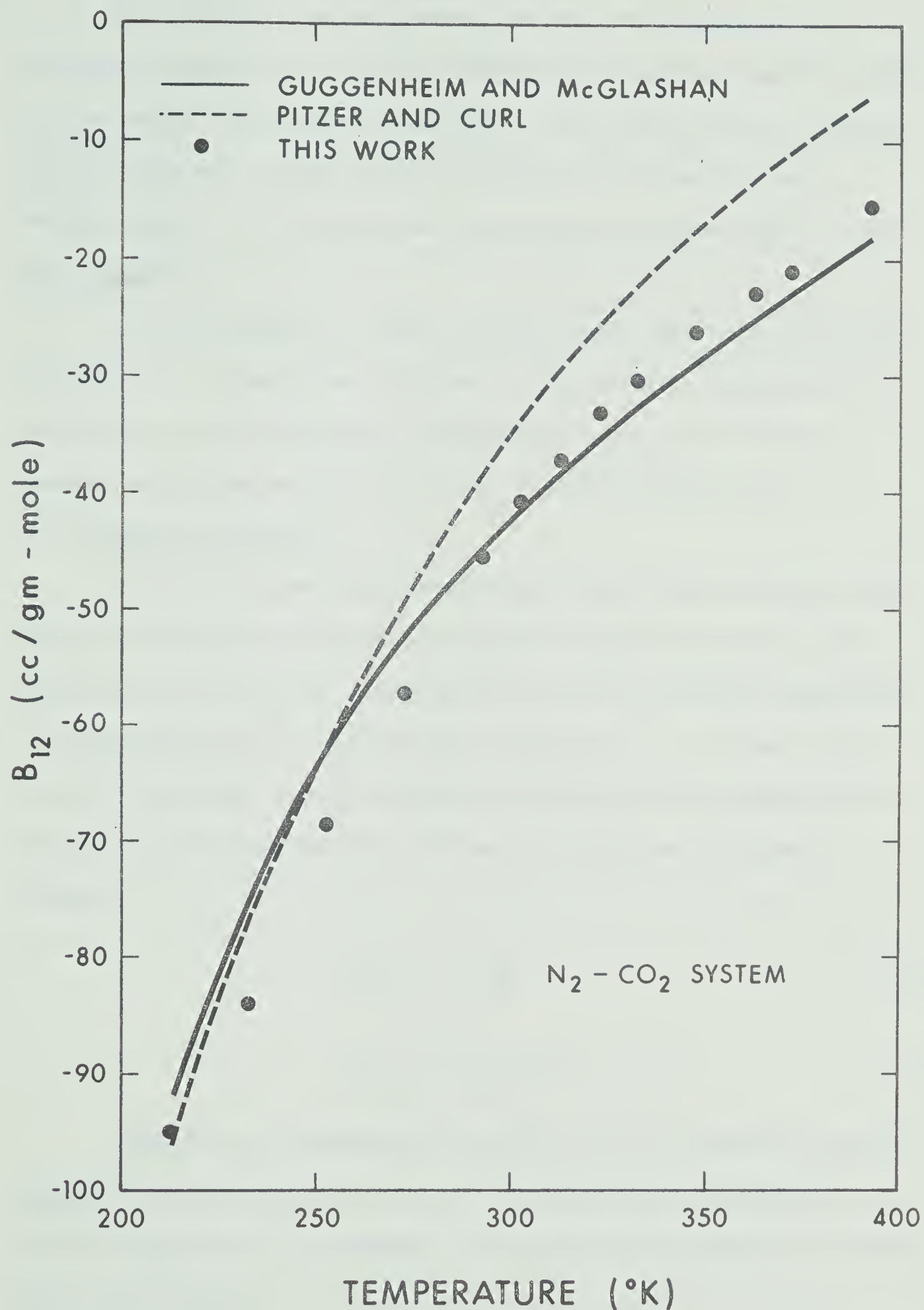


Figure 8. Comparison of B_{12} With Values Calculated From Corresponding States

For methane - carbon dioxide systems, the Guggenheim and McGlashan correlation is always slightly more negative than this work in the temperature range of this work. The Pitzer and Curl correlation is much more negative than this work at low temperatures, becomes closer as the temperature increases, and after 350°K, it is less negative.

For the nitrogen - carbon dioxide system, the Pitzer and Curl correlation is always less negative than this work. Guggenheim and McGlashan is less negative at temperatures lower than 310°K and becomes more negative than this work at higher temperatures.

B. Molecular Potential

It is well known that two molecules repel each other when they come close together and attract each other when they are far apart. The force of interaction F between two spherical non-polar molecules is a function of the intermolecular separation r . It is more convenient to use the potential energy of interaction $\phi(r)$ rather than the force of interaction $F(r)$. These two functions are simply related:

$$F(r) = - \frac{d\phi}{dr} \quad (22)$$

$$\phi(r) = \int_r^{\infty} F(r) dr \quad (23)$$

Theoretical considerations suggest that the repulsive potential should be an exponential function of intermolecular separation, but it is more convenient¹ to represent the repulsive potential by an inverse-power Law of type,

$$\phi(r) = \frac{\alpha}{r^n} \quad (24)$$

where α is a positive constant and n is a number usually taken to be between 8 and 6.

In order to take both repulsive and attractive forces between nonpolar molecules into account, it is customary to assume that the total potential energy is the sum of the two separate potentials:

$$\begin{aligned} \phi(r) &= \phi(r)_{\text{repulsive}} + \phi(r)_{\text{attractive}} \\ &= \frac{\alpha}{r^n} - \frac{\beta}{r^m} \end{aligned} \quad (25)$$

where α , β , n and m are positive constants and where $n > m$. This equation was first proposed by Mie⁴¹ and was extensively investigated by Lennard-Jones.

Equation (25) gives the potential energy of two molecules as a function of their separation and it is apparent that at some distance r^* , this energy is a minimum; this minimum energy is designated by $\phi(r)^*$. By algebraic rearrangement, Mie's potential can be written as

$$\phi(r) = \frac{\epsilon (n/m)^{\frac{1}{n-m}}}{n-m} \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right] \quad (26)$$

where $\epsilon = -\phi(r)^*$ and σ is the intermolecular distance when $\phi(r) = 0$.

Figure 9 shows the shape of the potential function.

The relation of second virial coefficients to the inter-

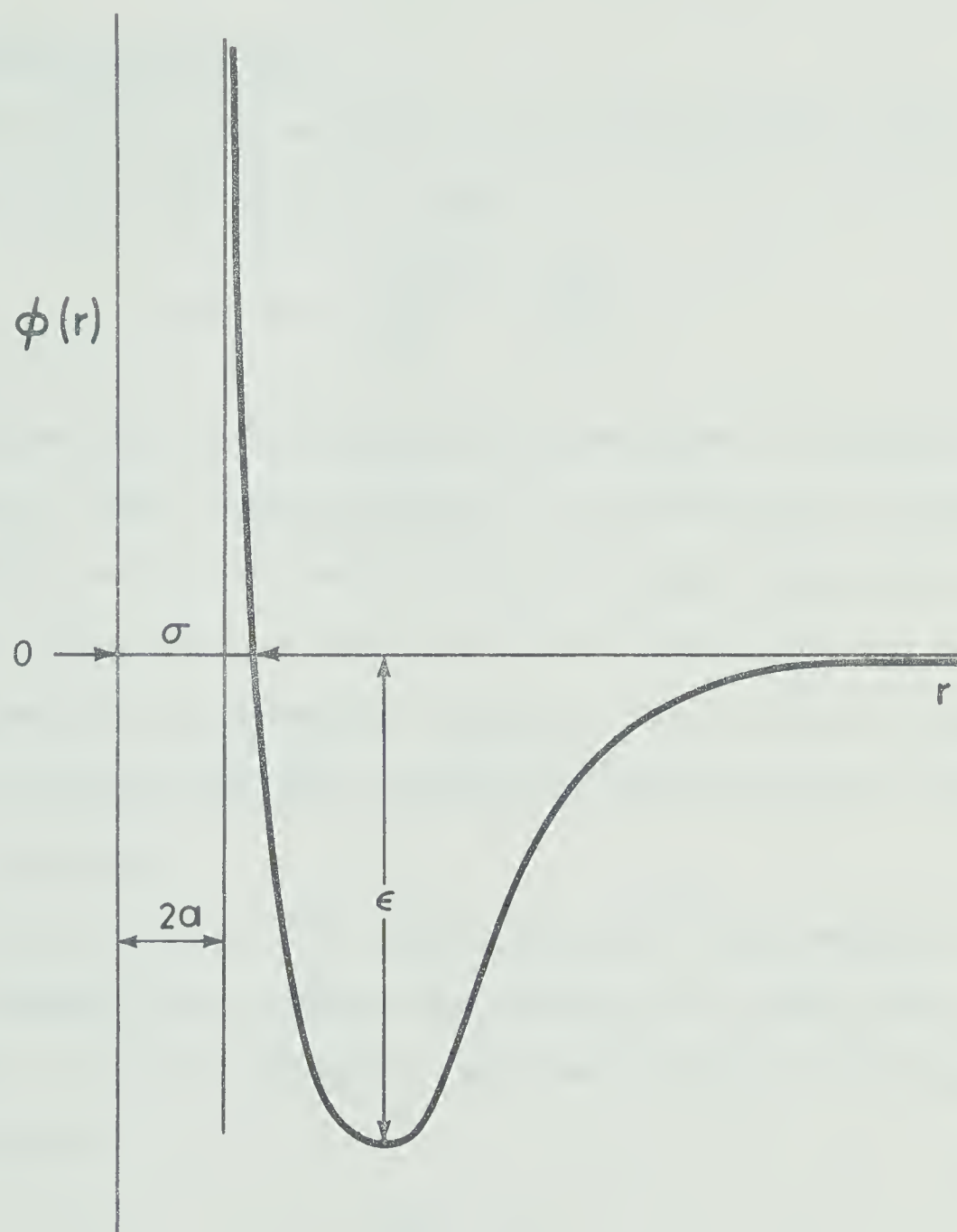


Figure 9. Potential Function With Adjustable Parameter

molecular potential function, $\phi(r)$ which is shown in equation (4) is as follows:

$$B = \int_0^{\infty} (1 - \exp[-\phi(r)/kT]) db_0(r)$$

1. Lennard-Jones Potential

The Lennard-Jones potential is the form when Mie's potential is rewritten with $n = 12$ and $m = 6$, then

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (27)$$

This equation gives what is probably the best-known two-parameter potential for small nonpolar molecules. In Lennard-Jones' formula, the repulsive wall is not vertical but has a finite slope; this implies that if two molecules have very high kinetic energy, they may be able to interpenetrate to separations smaller than the collision diameter σ . Potential functions with this property are sometimes called "soft-sphere" potentials.

Force constants, ϵ/k , σ and b_0 are given²¹ and numerical results based on Lennard-Jones potential are available for second virial coefficients²¹. It can be extended to mixtures by means of simple empirical mixing rules as

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \quad (28)$$

and

$$\epsilon_{12} = (\epsilon_1 \cdot \epsilon_2)^{1/2} \quad (29)$$

2. Kihara Potential

According to Lennard-Jones' potential, molecules consist of point centers surrounded by "soft" (i.e. penetrable) electron clouds. An alternate picture of molecules which was proposed by Kihara is to think of them as possessing impenetrable (hard) cores surrounded by penetrable electron clouds. In crude mechanical terms, Kihara's model (for spherically symmetric molecules) considers a molecule to be a hard billiard ball with a foam-rubber coat. Kihara^{35,26} writes a potential function identical to that of Lennard-Jones, except that the intermolecular distance is taken not as that between molecular centers but rather as the minimum distance between the surfaces of the molecular cores. The Kihara potential with three parameters is:

$$\left. \begin{aligned} \phi(r) &= \infty && \text{for } r < 2a \\ \phi(r) &= 4\epsilon \left[\left(\frac{\sigma-2a}{r-2a} \right)^{12} - \left(\frac{\sigma-2a}{r-2a} \right)^6 \right] && \text{for } r \geq 2a \end{aligned} \right\} \quad (30)$$

where $2a$ is molecular core diameter.

Prausnitz and Myers⁴⁶ have shown that the calculation of second virial coefficients by means of the Kihara potential agrees with some experimental data. The parameters for Kihara potential have been determined by Prausnitz and Myers from precision P-v-T data. When applied to mixtures, the interaction second virial coefficient was calculated from the following equation according to the Kihara potential,

$$B = \frac{2}{3} \pi N \sigma^3 \left[a^{*3} + 3 \left(2^{\frac{1}{6}} \right) a^{*2} F_1(T^*) + 3 \left(2^{\frac{1}{3}} \right) a^* F_2(T^*) + \left(2^{\frac{1}{3}} \right) F_3(T^*) \right] [1 + a^*]^{-3} \quad (31)$$

in which $T^* = kT/\epsilon$ and $a^* = \frac{2a}{\sigma - 2a}$

The mixing rules are:

$$T_{12}^* = (T_1^* \cdot T_2^*)^{\frac{1}{2}} \quad (32)$$

and

$$a_{12}^* = \frac{1}{2}(a_1^* + a_2^*) \quad (33)$$

Tables of $F_1(T^*)$, $F_2(T^*)$ and $F_3(T^*)$ are given by Hirschfelder, Curtiss and Bird²¹.

3. Comparison of Results

The calculated results from Lennard-Jones potential and the computer results of Kihara potential for methane - nitrogen, methane - carbon dioxide and nitrogen - carbon dioxide systems are given in Tables XV, XVI, and XVII respectively. These data are plotted in Figures 10, 11 and 12 for methane - nitrogen, methane - carbon dioxide, and nitrogen - carbon dioxide systems respectively for comparison with the results of this work.

For the methane - nitrogen system, the Kihara potential has a better comparison than the Lennard-Jones potential with this work. But the Pitzer and Curl correlation is the best among the four theoretical predictions to describe this system with the temperature

TABLE XV

Interaction Second Virial Coefficients of Methane - Nitrogen
Mixtures From This Work, Lennard-Jones and Kihara Potentials

(cc/gm-mole)

<u>Temperature ($^{\circ}$K)</u>	<u>This Work</u>	<u>Lennard-Jones</u>	<u>Kihara</u>
173.15	-87.32	-92.43	-91.02
193.15	-68.05	-73.79	-71.46
213.15	-53.91	-59.20	-56.93
233.15	-42.36	-47.56	-45.90
253.15	-33.42	-38.03	-36.33
273.15	-26.72	-30.08	-28.95
293.15	-19.58	-23.31	-22.74
313.15	-15.12	-17.63	-17.11
333.15	-10.59	-12.66	-12.45
353.15	- 7.14	- 8.34	- 8.53
373.15	- 5.14	- 4.55	- 5.13
393.15	- 2.47	- 1.19	- 2.08

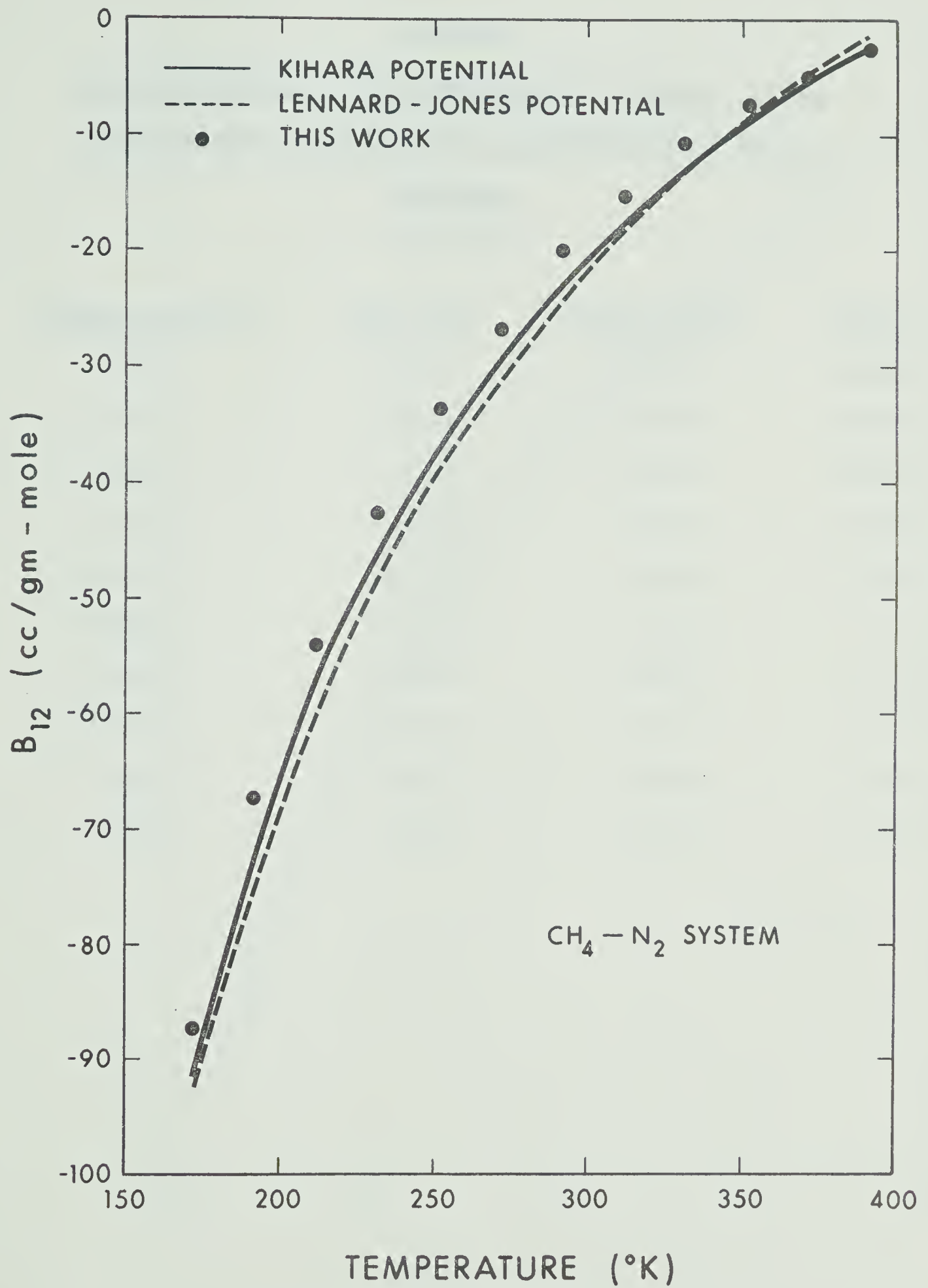


Figure 10. Comparison of B_{12} With Values Calculated From Molecular Potentials

TABLE XVI

Interaction Second Virial Coefficients of Methane - Carbon
Dioxide Mixtures From This Work, Lennard-Jones and Kihara

<u>Potentials</u>			
(cc/gm-mole)			
<u>Temperature (^oK)</u>	<u>This Work</u>	<u>Lennard-Jones</u>	<u>Kihara</u>
213.15	-136.74	-158.06	-153.74
233.15	-114.94	-133.00	-128.06
253.15	- 97.55	-112.94	-106.40
273.15	- 81.24	- 96.41	- 89.39
293.15	- 67.25	- 82.49	- 76.25
313.15	- 57.33	- 70.60	- 65.47
333.15	- 48.49	- 60.49	- 55.23
353.15	- 43.14	- 51.71	- 48.03
373.15	- 36.56	- 43.85	- 40.34
393.15	- 33.26	- 37.01	- 33.75

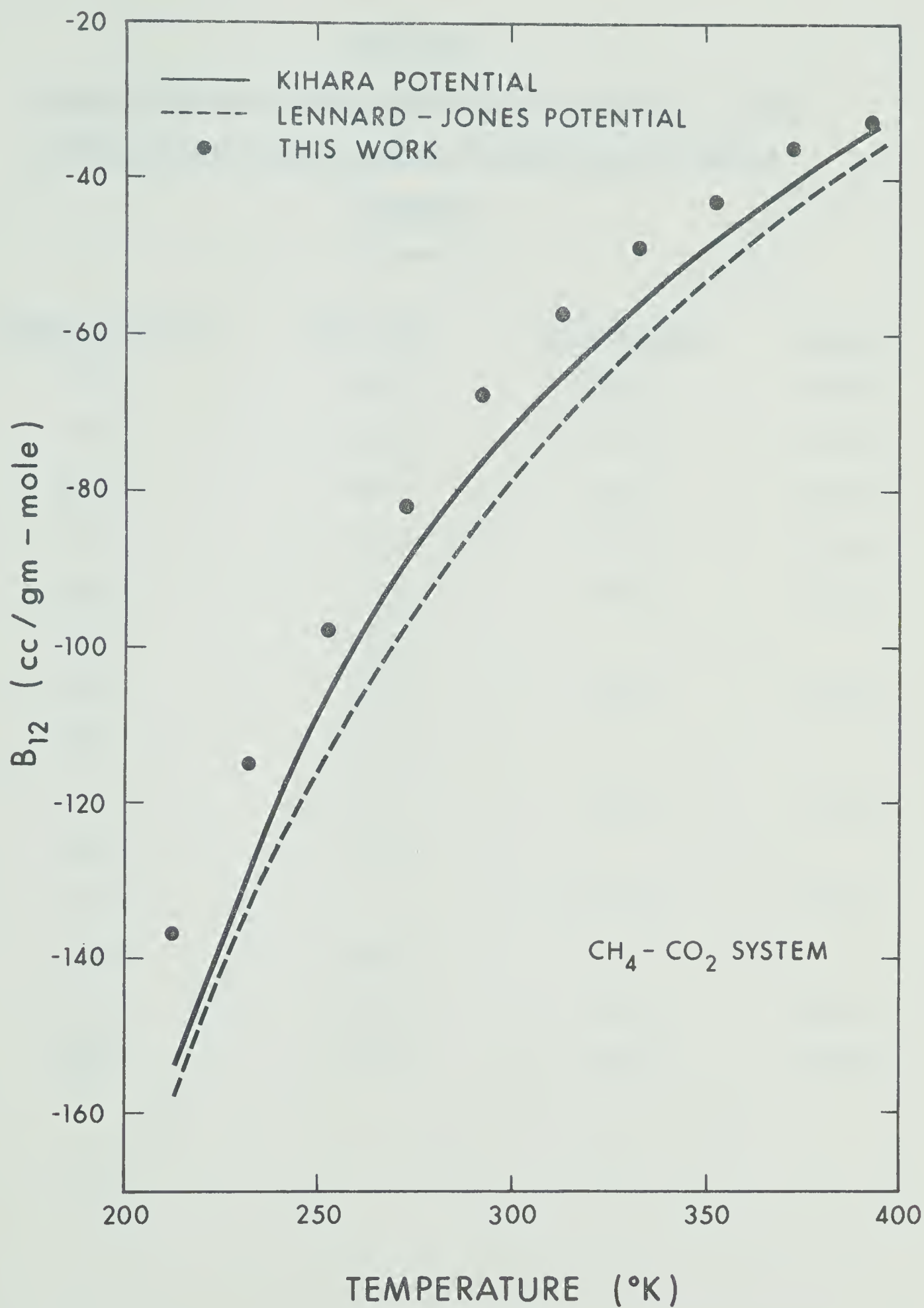


Figure 11. Comparison of B_{12} With Values Calculated from Molecular Potentials

TABLE XVII

Interaction Second Virial Coefficients of Nitrogen - Carbon

Dioxide Mixtures From This Work, Lennard-Jones and Kihara

Potentials

(cc/gm-mole)

<u>Temperature ($^{\circ}$K)</u>	<u>This Work</u>	<u>Lennard-Jones</u>	<u>Kihara</u>
213.15	-95.14	-95.63	-92.08
233.15	-83.99	-78.95	-74.91
253.15	-68.93	-65.35	-61.07
273.15	-57.28	-54.07	-50.56
293.15	-45.70	-44.61	-40.66
303.15	-40.98		
313.15	-37.26	-36.42	-33.07
323.15	-33.28		
333.15	-30.47	-29.46	-25.89
348.15	-26.18		
353.15		-23.32	-19.98
363.15	-22.91		
373.15	-20.71	-17.99	-16.23
393.15	-15.56	-13.23	-11.34

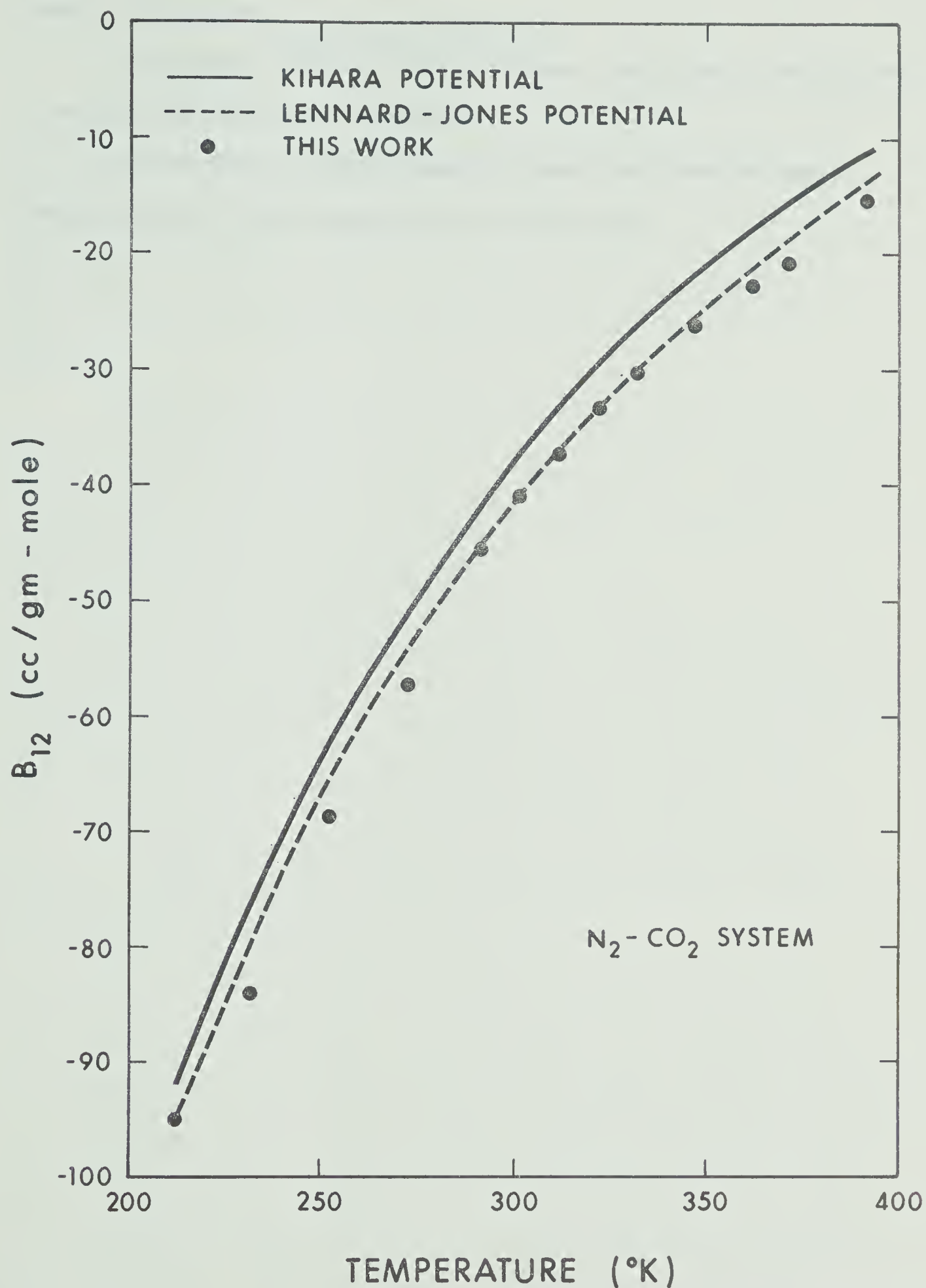


Figure 12. Comparison of B_{12} With Values Calculated from Molecular Potentials

range of this work.

For methane - carbon dioxide systems, the Kihara potential has a better comparison with this work.

For nitrogen - carbon dioxide systems, the Lennard-Jones potential has a better comparison with this work.

SUMMARY AND CONCLUSIONS

1. The modification of the original Knobler's design for direct measurement of interaction second virial coefficients has been made. The experiment was carried out at 2 atm. pressure in the temperature range between -100°C and 120°C . The second virial coefficient of carbon dioxide was determined between 0°C and -60°C by the same equipment.
2. A study has been done for the systems of methane - nitrogen, methane - carbon dioxide and nitrogen - carbon dioxide. Comparison was made with other results in literature by direct measurement of interaction second virial coefficient.
3. The P-v-T data of mixtures of methane - nitrogen, methane - carbon dioxide, and nitrogen - carbon dioxide have been extrapolated to obtain B_M , and B_{12} were then calculated by means of equation (2). Three sets of results were in very good agreement with this work.
4. The comparison of interaction second virial coefficients of methane - nitrogen, methane - carbon dioxide and nitrogen - carbon dioxide between this work and correlations based on the principle of corresponding states, those of Guggenheim and McGlashan, and Pitzer and Curl had been made. For the methane - nitrogen system, the Pitzer and Curl correlation gave better agreement with this work. For the methane - carbon dioxide system, the Guggenheim and McGlashan correlation gave better agreement at temperatures below 300°K , while the correlation of Pitzer and Curl was in good comparison at temperatures above 300°K . For the nitrogen - carbon dioxide system, the correlation of Guggenheim and McGlashan was in better agreement with

this work.

5. Interaction second virial coefficients calculated from Lennard-Jones potential and Kihara potential have been studied and the comparison with this work was made. For the methane - nitrogen and the methane - carbon dioxide systems, the Kihara potential gave the better prediction. For the nitrogen - carbon dioxide system, the Lennard-Jones potential was in good agreement with this work.

6. Comparisons were difficult to make because the reported second virial coefficients were not consistent in the literature, especially second virial coefficients of pure carbon dioxide. Results which used the same pure second virial coefficients as this work derived from P-v-T data of other workers were in good agreement with this work. The lack of agreement between the experimental results and those calculated from the principle of corresponding states and from molecular potentials may be due to the mixing rules used to calculate the parameters. The validity of these mixing rules should be tested by calculating the mixture parameters from the present experimental data and determining the form of the mixing rule.

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APPENDIX A

CALIBRATIONS

I. Calibration Data for 8163 model platinum resistance Thermometers
(Serial Nos. 1724262, 1752229)

This thermometer was calibrated for use in the range
 $90.188^{\circ}\text{K} < T < 773.15^{\circ}\text{K}$ ($-182.962^{\circ}\text{C} < t < 500.60^{\circ}\text{C}$) on the International practical temperature scale of 1968.

For $13.81^{\circ}\text{K} < T < 273.15^{\circ}\text{K}$

$$W = W_{\text{cct}} + dw$$

where $W = R/R(0^{\circ}\text{C})$ and W_{cct} is a reference function, independent of any particular thermometer.

For $90.188^{\circ}\text{K} < T < 273.16^{\circ}\text{K}$

$$dw = A_4 t + C_4 (t - 100) t^3$$

For $0^{\circ}\text{C} < t < 630.74^{\circ}\text{C}$

$$t = t' + dt$$

where

t' is determined by

$$w = 1 + A t' + B (t')^2$$

and

$$dt' = 0.45(t'/100) \left(\frac{t'}{100} - 1 \right) \left(\frac{t'}{419.58} - 1 \right) \left(\frac{t'}{630.74} - 1 \right)$$

The coefficient in the above relations were found by fixed-point calibrations, i.e. triple point of water, the steam or tin point and the zinc point using continuous thermometer currents of 1 and 2 mA.

For Serial No. 1724262

	0 mA	2 mA
A =	3.98556×10^{-3}	3.98553×10^{-3}
B =	-5.87665×10^{-7}	-5.87775×10^{-7}
A ₄ =	7.2864×10^{-7}	6.7345×10^{-7}
C ₄ =	1.1035×10^{-14}	1.1382×10^{-14}

For Serial No. 1752229

	0 mA	2 mA
A =	3.98468×10^{-3}	3.98465×10^{-3}
B =	-5.87540×10^{-7}	-5.87660×10^{-7}
A4 =	-1.0425×10^{-7}	-1.5988×10^{-7}
C4 =	8.1559×10^{-15}	8.5156×10^{-15}

$R(0^{\circ}\text{C}) = 25.5 \text{ ohms (approximately.)}$

II. Calibration of oil density for manometer

Kind of oil: cencoil-B

Temperature: 20°C

Run 1

Weight of bottle (50 c.c.) 20.6541 gm

Weight of bottle and oil 69.6642 gm

weight of oil = 49.0101 gm

Run 2

Weight of bottle 20.6584 gm

Weight of bottle and oil 69.6547 gm

weight of oil = 48.9983 gm

Average weight of oil (50 c.c. at 20°C) = 49.0042 gm

Density of oil = 0.9801 gm/c.c.

APPENDIX B

EXPERIMENTAL DATA

TABLE XVIII

RAW DATA FOR METHANE-NITROGEN SYSTEM

T (K)	P (MM HG)	ΔP (MM OIL)	B11*	B22*	C111*	C222*	E (N)*	B12*
173.15	1419.0	14.96	-145.00	-51.00	4900.	2250.	10.66	-87.33
173.15	1419.0	14.99	-145.00	-51.00	4900.	2250.	10.68	-87.31
193.15	1418.0	11.40	-116.00	-39.00	4300.	2000.	9.30	-68.19
193.15	1425.0	11.85	-116.00	-39.00	4300.	2000.	9.58	-67.91
213.15	1417.0	8.70	-94.50	-29.00	3860.	1900.	7.96	-53.78
213.15	1410.0	8.35	-94.50	-29.00	3860.	1900.	7.71	-54.03
233.15	1422.0	7.55	-78.00	-21.50	3450.	1800.	7.59	-42.15
233.15	1428.0	7.20	-78.00	-21.50	3450.	1800.	7.17	-42.57
253.15	1421.5	6.25	-65.00	-15.50	3050.	1700.	6.87	-33.37
253.15	1437.0	6.30	-65.00	-15.50	3050.	1700.	6.78	-33.46
273.15	1450.0	4.95	-54.50	-10.50	2700.	1500.	5.66	-26.83
273.15	1438.0	5.00	-54.50	-10.50	2700.	1500.	5.82	-26.67
273.15	1435.0	5.00	-54.50	-10.50	2700.	1500.	5.84	-26.65
293.15	1440.0	4.90	-45.00	-5.80	2600.	1250.	6.14	-19.25
293.15	1446.0	4.65	-45.00	-5.80	2600.	1250.	5.77	-19.62
293.15	1445.0	4.45	-45.00	-5.80	2600.	1250.	5.53	-19.86
313.15	1434.5	3.40	-37.50	-2.00	2390.	1250.	4.59	-15.15
313.15	1435.5	3.45	-37.50	-2.00	2390.	1250.	4.65	-15.09
333.15	1444.0	3.10	-31.00	1.00	2250.	1250.	4.40	-10.59
333.15	1415.0	2.98	-31.00	1.00	2250.	1250.	4.41	-10.58
353.15	1434.0	2.50	-26.00	3.80	2140.	1200.	3.82	-7.27
353.15	1443.0	2.70	-26.00	3.80	2140.	1200.	4.08	-7.01
373.15	1448.0	1.25	-21.00	6.00	2120.	1200.	1.97	-5.52
373.15	1444.0	1.75	-21.00	6.00	2120.	1200.	2.79	-4.70
373.15	1427.0	1.35	-21.00	6.00	2120.	1200.	2.19	-5.30
393.15	1430.0	1.00	-16.50	8.20	1880.	1150.	1.70	-2.44
393.15	1419.0	0.95	-16.50	8.20	1880.	1150.	1.64	-2.50

*B: cc/gm-mole C: (cc/gm-mole)² E: cc/gm-mole

TABLE XIX
RAW DATA FOR METHANE-CARBON DIOXIDE SYSTEM

T(K)	P(MM HG)	Δ (MM OIL)	B11	B22	C111	C222	E(N)	B12
213.15	1428.0	48.71	-262.00	-94.50	1000.	3860.	42.38	-135.86
213.15	1401.0	44.95	-262.00	-94.50	1000.	3860.	40.63	-137.61
233.15	1433.0	32.17	-214.00	-78.00	4700.	3450.	30.92	-115.07
233.15	1432.0	32.37	-214.00	-78.00	4700.	3450.	31.17	-114.82
253.15	1431.0	23.73	-180.00	-65.00	5600.	3050.	25.16	-97.33
253.15	1427.0	23.20	-180.00	-65.00	5600.	3050.	24.73	-97.76
273.15	1441.0	18.60	-150.00	-54.50	5750.	2700.	21.22	-81.02
273.15	1434.0	18.05	-150.00	-54.50	5750.	2700.	20.79	-81.45
293.15	1433.0	15.20	-127.00	-45.00	4600.	2600.	18.97	-67.02
293.15	1448.0	15.15	-127.00	-45.00	4600.	2600.	18.51	-67.48
313.15	1435.0	12.30	-110.00	-37.50	4600.	2390.	16.43	-57.31
313.15	1442.5	12.40	-110.00	-37.50	4600.	2390.	16.39	-57.35
333.15	1429.0	10.15	-95.00	-31.00	4400.	2250.	14.61	-48.38
333.15	1425.0	9.95	-95.00	-31.00	4400.	2250.	14.40	-48.59
353.15	1438.0	7.60	-83.50	-26.00	3900.	2140.	11.47	-43.27
353.15	1416.0	7.55	-83.50	-26.00	3900.	2140.	11.76	-42.98
373.15	1428.5	6.55	-73.00	-21.00	3400.	2120.	10.62	-36.37
373.15	1429.0	6.30	-73.00	-21.00	3400.	2120.	10.20	-36.79
373.15	1415.5	6.35	-73.00	-21.00	3400.	2120.	10.48	-36.51
393.15	1432.0	3.55	-62.00	-16.50	2900.	1880.	6.03	-33.21
393.15	1433.0	3.50	-62.00	-16.50	2900.	1880.	5.93	-33.31

TABLE XX

RAW DATA FOR NITROGEN-CARBON DIOXIDE SYSTEM

T(K)	P(MM HG)	ΔP (MM OIL)	B11	B22	C111	C222	E(N)	B12
213.15	1404.5	56.44	-262.00	-29.00	1000.	1900.	50.07	-95.42
213.15	1409.0	57.42	-262.00	-29.00	1000.	1900.	50.63	-94.86
233.15	1424.0	35.00	-214.00	-21.50	4700.	1800.	33.44	-84.30
233.15	1412.0	35.00	-214.00	-21.50	4700.	1800.	34.07	-83.67
253.15	1402.0	26.02	-180.00	-15.50	5600.	1700.	28.36	-69.38
253.15	1419.0	27.48	-180.00	-15.50	5600.	1700.	29.25	-68.49
273.15	1428.0	20.00	-150.00	-10.50	5750.	1500.	22.92	-57.32
273.15	1440.0	20.30	-150.00	-10.50	5750.	1500.	22.87	-57.37
273.15	1415.0	19.76	-150.00	-10.50	5750.	1500.	23.08	-57.16
293.15	1437.0	16.75	-127.00	-5.80	4600.	1250.	20.56	-45.83
293.15	1456.0	17.60	-127.00	-5.80	4600.	1250.	21.05	-45.34
293.15	1456.0	17.00	-127.00	-5.80	4600.	1250.	20.31	-46.08
293.15	1442.0	17.10	-127.00	-5.80	4600.	1250.	20.85	-45.54
303.15	1334.0	13.50	-118.00	-4.00	4600.	1250.	20.03	-40.96
303.15	1341.0	13.70	-118.00	-4.00	4600.	1250.	20.11	-40.88
303.15	1347.7	13.60	-118.00	-4.00	4600.	1250.	19.76	-41.23
303.15	1352.8	13.85	-118.00	-4.00	4600.	1250.	19.97	-41.02
303.15	1344.0	13.50	-118.00	-4.00	4600.	1250.	19.72	-41.27
303.15	1336.0	13.85	-118.00	-4.00	4600.	1250.	20.50	-40.49
313.15	1341.0	12.40	-110.00	-2.00	4600.	1250.	18.85	-37.14
313.15	1352.0	12.40	-110.00	-2.00	4600.	1250.	18.54	-37.45
313.15	1345.0	12.45	-110.00	-2.00	4600.	1250.	18.82	-37.17
323.15	1343.0	10.90	-102.00	-0.40	4500.	1250.	17.09	-34.10
323.15	1358.0	11.80	-102.00	-0.40	4500.	1250.	18.11	-33.08
323.15	1357.0	11.17	-102.00	-0.40	4500.	1250.	17.15	-34.04
323.15	1328.0	11.50	-102.00	-0.40	4500.	1250.	18.47	-32.72

TABLE XX (CONTINUED)
RAW DATA FOR NITROGEN-CARBON DIOXIDE SYSTEM

T(K)	P(MM HG)	ΔP (MM OIL)	B11	B22	C111	C222	E(N)	B12
333.15	1361.0	10.35	-95.00	1.00	4400.	1250.	16.32	-30.67
333.15	1313.0	10.15	-95.00	1.00	4400.	1250.	17.23	-29.76
333.15	1297.0	9.00	-95.00	1.00	4400.	1250.	15.64	-31.35
333.15	1329.0	9.96	-95.00	1.00	4400.	1250.	16.50	-30.49
333.15	1331.0	10.30	-95.00	1.00	4400.	1250.	17.01	-29.98
333.15	1340.0	10.40	-95.00	1.00	4400.	1250.	16.94	-30.05
333.15	1324.0	9.60	-95.00	1.00	4400.	1250.	16.00	-30.99
333.15	1334.0	10.05	-95.00	1.00	4400.	1250.	16.51	-30.48
348.15	1317.0	8.70	-86.00	3.00	4000.	1250.	15.37	-26.12
348.15	1318.0	8.40	-86.00	3.00	4000.	1250.	14.81	-26.68
348.15	1334.0	8.90	-86.00	3.00	4000.	1250.	15.32	-26.17
348.15	1338.0	9.20	-86.00	3.00	4000.	1250.	15.75	-25.74
363.15	1339.0	7.00	-78.00	5.00	3800.	1200.	12.48	-24.01
363.15	1328.0	7.55	-78.00	5.00	3800.	1200.	13.71	-22.78
363.15	1330.0	7.50	-78.00	5.00	3800.	1200.	13.58	-22.91
363.15	1325.0	7.50	-78.00	5.00	3800.	1200.	13.68	-22.81
363.15	1334.0	7.50	-78.00	5.00	3800.	1200.	13.49	-23.00
363.15	1328.0	7.40	-78.00	5.00	3800.	1200.	13.43	-23.06
373.15	1342.0	6.95	-73.00	6.00	3500.	1200.	12.71	-20.78
373.15	1321.0	6.65	-73.00	6.00	3500.	1200.	12.55	-20.94
373.15	1325.0	6.65	-73.00	6.00	3500.	1200.	12.49	-21.01
393.15	1360.0	6.05	-62.00	8.20	3000.	1150.	11.39	-15.50
393.15	1338.0	5.90	-62.00	8.20	3000.	1150.	11.47	-15.42
393.15	1346.0	5.80	-62.00	8.20	3000.	1150.	11.14	-15.75

ERROR ANALYSIS

1. The temperatures were controlled within $\pm 0.01^{\circ}\text{C}$ for each temperature level. This can introduce an error in excess second virial coefficient of ± 0.06 percent at low temperature regions and ± 0.03 percent at high temperature regions for methane - nitrogen systems. For methane - carbon dioxide system, ± 0.4 percent at low temperature region and ± 0.2 percent at high temperature region. For nitrogen - carbon dioxide system, ± 0.8 percent at low temperature region and ± 0.06 percent at high temperature region.

2. In this work, pressure reading is within 0.05 mm oil and using first term of equation (9), as

$$dE = \left(\frac{2RT}{P^2} \right) d(\Delta P)$$

For $P = 2$ atm., the maximum error for excess second virial coefficients is 0.06 cc/gm-mole at 25°C which means that the pressure reading error at low temperatures is relatively lower than that at high temperatures. This will give the maximum error of 3 percent.

3. The largest change in volume of the oil manometer movement is 0.03 cc. This will cause the pressure change of 0.6 mm oil and it may introduce an error of less than 1 percent in the pressure reading.

4. The error due to the impurity in the pure gas is negligibly small.

5. The error due to the solubility of gases in the manometer oil is negligible.

6. The relative error in reproducibility of the experiment is between 0.1 and 4 percent.

APPENDIX D

DERIVATION OF EQUATION USED

Derivation of Equation (9)

Write the pressure of a gas P, in terms of B, C and density d.

$$P = RTd(1 + Bd + cd^2) \quad (D.1)$$

Thus for the ratio of final to initial pressure,

$$\frac{P_f}{P} = \frac{d_f(1 + B_f d_f + C_f d_f^2)}{d_i(1 + B_i d_i + C_i d_i^2)} \quad (D.2)$$

since pressure in the bulbs before mixing are equal,

$$\begin{aligned} P &= d_1(1 + B_{11}d_1 + C_{111}d_1^2) \\ &= d_2(1 + B_{22}d_2 + C_{222}d_2^2) \end{aligned} \quad (D.3)$$

Neglecting the effect of the pressure change on the density of the gas that is at room temperature,

then

$$d_f = \frac{d_1 + d_2}{2} \quad (D.4)$$

The mole fractions y_1 and y_2 of the mixed gases may be expressed in terms of d_1 and d_2 :

$$y_1 = \frac{d_1}{d_1 + d_2}$$

$$y_2 = \frac{d_2}{d_1 + d_2}$$

so,

$$B_f = \left(\frac{d_1}{d_1+d_2} \right)^2 B_{11} + 2 \frac{d_1 d_2}{(d_1+d_2)^2} B_{12} + \left(\frac{d_2}{d_1+d_2} \right)^2 B_{22}$$

substitute

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}) - E$$

then,

$$B_f = \left(\frac{d_1}{d_1+d_2} \right) B_{11} + 2 \frac{d_1 d_2}{(d_1+d_2)^2} E + \left(\frac{d_2}{d_1+d_2} \right) B_{22} \quad (D.5)$$

and

$$\begin{aligned} C_f = & \left(\frac{d_1}{d_1+d_2} \right)^3 C_{111} + 3 \left(\frac{d_1}{d_1+d_2} \right)^2 \left(\frac{d_2}{d_1+d_2} \right) C_{112} \\ & + 3 \left(\frac{d_1}{d_1+d_2} \right) \left(\frac{d_2}{d_1+d_2} \right)^2 C_{122} + \left(\frac{d_2}{d_1+d_2} \right)^3 C_{222} \end{aligned} \quad (D.6)$$

since

$$\Delta P = P_f - P$$

Thus

$$\frac{\Delta P}{P} = \frac{P_f}{P} - 1$$

$$= \frac{d_f (1 + B_f d_f + C_f d_f^2)}{d_1 (1 + B_{11} d_1 + C_{111} d_1^2)} - 1 \quad (D.7)$$

Substitute Equation (D.4), (D.5), and (D.6) into (D.7) and after rearrangement,

$$\begin{aligned}
\frac{\Delta P}{P} = & \frac{(d_2 - d_1)^2}{4d_1 d_2} + \frac{d_2 E}{2(1 + B_{11}d_1 + C_{111}d_1^2)} \\
& + \frac{C_{111}(d_1 d_2^2 - d_1^3) + C_{222}(d_1^2 d_2 - d_2^3) + 3d_1 d_2 (d_1 G_1 + d_2 G_2)}{8d_1(1 + B_{11}d_1 + C_{111}d_1^2)}
\end{aligned}
\tag{D.8}$$

where

$$G_i = C_{iij} - \frac{1}{3} (2 C_{iii} + C_{jjj})$$

Rewrite equation (D.8)

$$\begin{aligned}
E = & 2 \left[\frac{\Delta P}{P} - \frac{(d_1 - d_2)^2}{4d_1 d_2} \right] \frac{P}{RT d_1 d_2} \\
& + \frac{(d_1^2 - d_2^2)(C_{111}d_1 - C_{222}d_2)}{4d_1 d_2} - \frac{3}{4}(d_1 G_1 + d_2 G_2)
\end{aligned}
\tag{D.9}$$

substitute for

$$d_i = \frac{P}{RT} - B_{ii} \left(\frac{P}{RT} \right)^2 + (2B_{ii}^2 - C_{iii}) \left(\frac{P}{RT} \right)^3 + \dots \tag{D.10}$$

Thus equation (D.9) becomes

$$\begin{aligned}
d_1 d_2 E = & 2\Delta PRT - \frac{(d_1 - d_2)^2}{2d_1 d_2} \left(\frac{P}{RT} \right) + \frac{1}{4} (d_1^2 - d_2^2) (C_{111}d_1 - C_{222}d_2) \\
& - \frac{3}{4} d_1 d_2 (d_1 G_1 + d_2 G_2)
\end{aligned}
\tag{D.11}$$

Then,

$$(d_1 - d_2) = (B_{22} - B_{11}) \left(\frac{P}{RT} \right)^2 + (-2B_{22}^2 + C_{222} + 2B_{11}^2 - C_{111}) \left(\frac{P}{RT} \right)^3 + \dots$$

$$(d_1 - d_2)^2 = (B_{22} - B_{11})^2 \left(\frac{P}{RT} \right)^4 + 2(B_{22} - B_{11})(-2B_{22}^2 + C_{222} + 2B_{11}^2 - C_{111}) \left(\frac{P}{RT} \right)^5 + \dots$$

$$(d_1^2 - d_2^2) = 2(B_{22} - B_{11}) \left(\frac{P}{RT} \right)^3 + (5B_{11}^2 - 5B_{22}^2 - 2C_{111} + 2C_{222}) \left(\frac{P}{RT} \right)^4 + \dots$$

$$\begin{aligned} d_1 d_2 &= \left(\frac{P}{RT} \right)^2 - (B_{11} + B_{22}) \left(\frac{P}{RT} \right)^3 + (2B_{11}^2 + 2B_{22}^2 + B_{11}B_{22} \\ &\quad - C_{111} - C_{222}) \left(\frac{P}{RT} \right)^4 + (B_{11}C_{222} + B_{22}C_{111} - 2B_{11}B_{22}^2 \\ &\quad - 2B_{11}^2B_{22}) \left(\frac{P}{RT} \right)^5 + \dots \end{aligned}$$

$$\begin{aligned} \frac{(d_1 d_2)^2}{d_1 d_2} &= (B_{22} - B_{11})^2 \left(\frac{P}{RT} \right)^2 + (B_{11} - B_{22})(3B_{22}^2 - 2C_{222} - 3B_{11}^2 \\ &\quad + 2C_{111}) \left(\frac{P}{RT} \right)^3 + \dots \end{aligned}$$

$$d_1 d_2 (d_1 G_1 + d_2 G_2) = (G_1 + G_2) \left(\frac{P}{RT} \right)^3 - \left[G_1 (2B_{11} + B_{22}) + G_2 (B_{11} + 2B_{22}) \right] \left(\frac{P}{RT} \right)^4 + \dots$$

$$(d_1^2 - d_2^2) (C_{111} d_1 - C_{222} d_2) = 2(B_{22} - B_{11}) (C_{111} - C_{222}) \left(\frac{P}{RT} \right)^4 + \dots$$

substitute these equations into equation (D.11)

$$\begin{aligned} E \left[\left(\frac{P}{RT} \right)^2 - (B_{11} + B_{22}) \left(\frac{P}{RT} \right)^3 + (2B_{11}^2 + 2B_{22}^2 + B_{11}B_{22} - C_{111} - C_{222}) \right. \\ \left. \left(\frac{P}{RT} \right)^4 + \dots \right] = \frac{2\Delta P}{RT} - \frac{1}{2} \left[(B_{22} - B_{11})^2 \left(\frac{P}{RT} \right)^2 + (B_{11} - B_{22}) \right. \\ \left. (3B_{22}^2 - 2C_{222} - 3B_{11}^2 + 2C_{111}) \left(\frac{P}{RT} \right)^3 + \dots \right] \left(\frac{P}{RT} \right) \\ + \frac{1}{4} \left[2(B_{22} - B_{11}) (C_{111} - C_{222}) \left(\frac{P}{RT} \right)^4 + \dots \right] \\ - \frac{3}{4} \left\{ (G_1 + G_2) \left(\frac{P}{RT} \right)^3 - \left[G_1 (2B_{11} + B_{22}) + G_2 (B_{11} + 2B_{22}) \right] \right. \\ \left. \left(\frac{P}{RT} \right)^4 + \dots \right\} \end{aligned} \quad (D.12)$$

rearrange equation (D.12)

$$\begin{aligned}
 E = & \frac{2RT\Delta P}{P^2} + \left\{ \begin{array}{l} + (B_{11} + B_{22}) E \\ - \frac{1}{2} (B_{22} - B_{11})^2 \\ - \frac{3}{4} (G_1 + G_2) \end{array} \right\} \left(\frac{P}{RT} \right) \\
 & + \left\{ \begin{array}{l} - E(2B_{11}^2 + 2B_{22}^2 + B_{11}B_{22} - C_{111} - C_{222}) \\ - \frac{1}{2}(B_{11}-B_{22})(3B_{22}^2 - 2C_{222} - 3B_{11}^2 + 2C_{111}) \\ - \frac{1}{2}(B_{22} - B_{11}) (C_{111} - C_{222}) \\ + \frac{3}{4} G_1(2B_{11} + B_{22}) + G_2(B_{11} + 2B_{22}) \end{array} \right\} \left(\frac{P}{RT} \right)^3 \\
 & + \dots
 \end{aligned}$$

Thus

$$\begin{aligned}
 E = & \frac{2RT\Delta P}{P^2} - 2 \left[(B_{11} - B_{22})^2/4 - E(B_{11} + B_{22})/2 + 3(G_1 + G_2)/8 \right] \left(\frac{P}{RT} \right) \\
 & - 2 \left\{ \frac{3}{4}(B_{11} - B_{22})[(C_{111} - B_{11}^2) - (C_{222} - B_{22}^2)] \right. \\
 & + \left(\frac{E}{2} \right) (2B_{11}^2 + B_{11}B_{22} + 2B_{22}^2 - C_{111} - C_{111}) \\
 & \left. - \frac{3}{8} [G_1(2B_{11} + B_{22}) + G_2(B_{11} + 2B_{22})] \right\} \left(\frac{P}{RT} \right)^2 + \dots \quad (9)
 \end{aligned}$$

APPENDIX E

DETERMINATION OF SECOND VIRIAL COEFFICIENT OF CARBON DIOXIDE

The virial equation of state can be expressed by an expansion using the pressure as the independent variable,

$$\frac{PV}{RT} = 1 + B'P + C'P^2 + \dots$$

using the first two terms of the expansion

$$\frac{PV}{RT} = 1 + B'P$$

where $B' = \frac{B}{RT}$

so $\frac{PV}{RT} = 1 + \frac{BP}{RT}$

or $V = \frac{RT}{P} + B$

In this work, volume is constant and equal between the two systems, then

$$\frac{RT_1}{P_{1He}} + B_{He} = \frac{RT_2}{P_{2He}} + B_{2He} \quad (E.1)$$

$$\frac{RT_1}{P_{1He}} + B_{1He} = \frac{RT_1}{P_{1CO_2}} + B_{1CO_2} \quad (E.2)$$

$$\frac{RT_2}{P_{2CO_2}} + B_{2CO_2} = \frac{RT_1}{P_{1CO_2}} + B_{1CO_2} \quad (E.3)$$

and $P_{1He} = P_{1CO_2} \quad (E.4)$

Equation (E.1), (E.2), (E.3), and (E.4) can be reduced to

$$\frac{RT_2}{P_{2\text{He}}} = \frac{RT_1}{P_{1\text{He}}} + B_{1\text{He}} - B_{2\text{He}}$$

$$P_{2\text{CO}_2} = P_{2\text{He}} + \Delta P$$

Thus

$$B_{2\text{CO}_2} = \frac{RT_1}{P_{1\text{CO}_2}} - \frac{RT_2}{P_{2\text{CO}_2}} + B_{1\text{CO}_2}$$

TABLE XXI

Raw Data For Second Virial Coefficient of Pure Carbon Dioxide

	<u>T(^oK)</u>	<u>P(mm Hg)</u>	<u>ΔP(mm oil)</u>	<u>B_{CO₂} (cc/gm-mole)</u>
Reference point	273.15	1429		-150.00
	263.15		-21.47	-163.50
	253.15		-46.05	-180.07
Reference point	253.15	1336		-180.07
	243.15		-26.50	-197.75
	233.15		-44.25	-210.89
Reference point	233.15	1259.5		-210.89
	223.15		-33.35	-244.12
	213.15		-70.10	-262.06

Values of B_{He} Used:

<u>T(^oK)</u>	<u>B_{He} (cc/gm-mole)</u>
273.15	11.825
253.15	11.880
233.15	11.950

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